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Locating and Estimating Air Emissions from Sources of 1,3-Butadiene

Radian Corp., Research Triangle Park, NC

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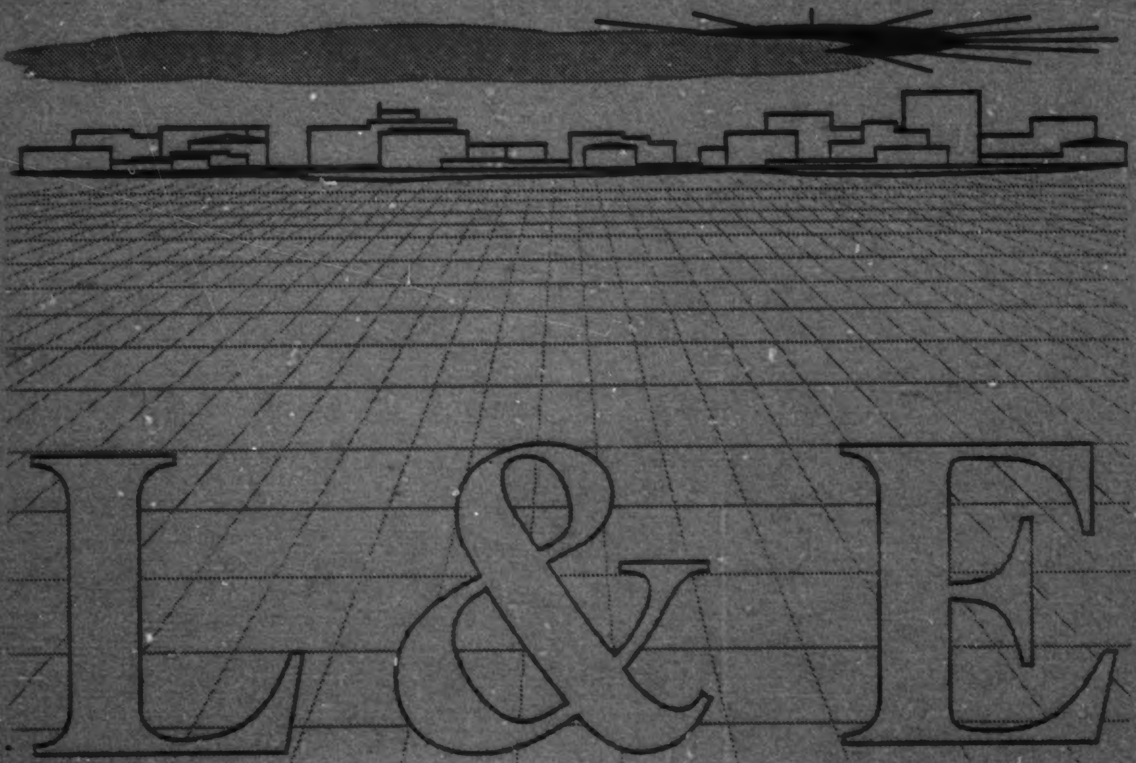

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16. ABSTRACT

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this to compile available information on sources and emissions of these substances. This document deals specifically with 1,3-butadiene. Its intended audience includes Federal, State and local air pollution personnel and others interested in locating potential emitters of 1,3-butadiene and in making gross estimates of air emissions therefrom.

This document presents information on (1) the types of sources that may emit 1,3,-butadiene, (2) process variations and release points that may be expected within these sources, and (3) available emissions information indicating the potential for 1,3-butadiene releases into the air from each operation.

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Contract Number 68-02-4392

EPA Project Officer: Anne A. Pope

U. S. ENVIRONMENTAL PROTECTION AGENCY

Office Of Air and Radiation
Office Of Air Quality Planning And Standards
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EPA 450/2-89-021

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SECTION 1
PURPOSE OF DOCUMENT

The U. S. Environmental Protection Agency (EPA), State, and local air pollution control agencies are becoming increasingly aware of the presence of substances in the ambient air that may be toxic at certain concentrations. This awareness, in turn, has led to attempts to identify source/receptor relationships for these substances and to develop control programs to regulate emissions. Unfortunately, very little information is available on the ambient air concentrations of these substances or about the sources that may be discharging them to the atmosphere.

To assist groups interested in inventorying air emissions of various potentially toxic substances, EPA is preparing a series of documents such as this that compiles available information on sources and emissions of these substances. Other documents in the series are listed below:

Substance	EPA Publication Number
Acrylonitrile	EPA-450/4-84-007a
Carbon Tetrachloride	EPA-450/4-84-007b
Chloroform	EPA-450/4-84-007c
Ethylene Dichloride	EPA-450/4-84-007d
Formaldehyde	EPA-450/4-84-007e
Nickel	EPA-450/4-84-007f
Chromium	EPA-450/4-84-007g
Manganese	EPA-450/4-84-007h
Phosgene	EPA-450/4-84-007i
Epichlorohydrin	EPA-450/4-84-007j
Vinylidene Chloride	EPA-450/4-84-007k
Ethylene Oxide	EPA-450/4-84-007l
Chlorobenzenes	EPA-450/4-84-007m
Polychlorinated Biphenyls (PCBs)	EPA-450/4-84-007n
Polycyclic Organic Matter (POM)	EPA-450/4-84-007p
Benzene	EPA-450/4-84-007q
Perchloroethylene and Trichloroethylene	EPA-450/2-89-013

This document deals specifically with 1,3-butadiene, commonly referred to as butadiene. Its intended audience includes Federal, State, and local air pollution personnel and others who are interested in locating potential emitters of 1,3-butadiene, and making gross estimates of air emissions therefrom.

Because of the limited availability of data on potential sources of 1,3-butadiene emissions and the variability in process configurations, control equipment, and operating procedure, amongst facilities, this document is best used as a primer to inform air pollution personnel about the (1) types of sources that may emit 1,3-butadiene, (2) process variations and release points that may be expected, and (3) available emissions information on the potential for 1,3-butadiene releases into the air. The reader is strongly cautioned against using the emissions information in this document to develop an exact assessment of emissions from any particular facility. Most estimates contained herein are values reported by the facilities in 1984 in response to EPA requests for information and are, therefore, somewhat out of date. Furthermore, not all facilities received requests, and those that received requests did not always provide complete responses. More recent data are now coming available which indicate higher levels of controls and lower emissions. The Agency is evaluating these data at this time. For more accurate estimates, the reader should seek more current and complete data.

It is possible, in some cases, that orders-of-magnitude differences may result between actual and estimated emissions, depending on differences in source configurations, control equipment, and operating practices. Thus, in all situations where an accurate assessment of 1,3-butadiene emissions is necessary, the source-specific information should be obtained to confirm the existence of particular emitting operations and the types and effectiveness of control measures, and to determine the impact of operating practices. A source test and/or material balance calculations should be considered as the best method of determining air emissions from an operation.

Most of the emission factors presented in the text are based on the 1984 data with the supporting facility-specific data provided in Appendix B.

The emission factors for equipment leaks were developed by the Chemical Manufacturers' Association (CMA) and are based on a 1989 study of equipment leak emissions at butadiene production facilities. Significantly different from the Synthetic Organic Chemical Manufacturing Industry (SOCMI) emission factors, these CMA factors were assumed to better represent equipment leak emissions at other butadiene users and were used to estimate annual emissions. Again, the reader should collect facility-specific data for the most accurate estimates. Other alternatives are also presented by any EPA publication "Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP."[1]

In addition to the information presented in this document, another potential source of emissions data for 1,3-butadiene is the Toxic Chemical Release Inventory (TRI) form required by Section 313 of Title III of the 1986 Superfund Amendments and Reauthorization Act (SARA 313).[2] SARA 313 requires owners and operators of facilities in certain Standard Industrial Classification Codes that manufacture, import, process or otherwise use toxic chemicals (as listed in Section 313) to report annually their releases of these chemicals to all environmental media. As part of SARA 313, EPA provides public access to the annual emissions data. The TRI data include general facility information, chemical information, and emissions data. Air emissions data are reported as total facility release estimates for fugitive emissions and point source emissions. No individual process or stack data are provided to EPA under the program. The TRI requires sources to use stack monitoring data for reporting, if available, but the rule does not require stack monitoring or other measurement of emissions if it is available. If monitoring data are unavailable, emissions are to be quantified based on best estimates of releases to the environment. The reader is cautioned that the TRI will not likely provide facility, emissions, and chemical release data sufficient for conducting detailed exposure modeling and risk assessment. In many cases, the TRI data are based on annual estimates of emissions (i.e., on emission factors, material balance calculations, and engineering judgment). We recommend the use of TRI data in conjunction with the information provided in this document to locate potential emitters of butadiene and to make preliminary estimates of air emissions from these facilities.

REFERENCES FOR SECTION 1

1. U. S. Environmental Protection Agency. Protocols for Generating Unit-Specific Emissions Estimates for Equipment Leaks of VOC and VHAP. EPA-450/3-88-010. Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina. October 1988.

2. Toxic Chemical Release Reporting: Community Right-To-Know. Federal Register 52 (107): 21152-21208. June 4, 1987.

SECTION 2
OVERVIEW OF DOCUMENT CONTENTS

As noted in Section 1, the purpose of this document is to assist Federal, State, and local air pollution agencies and others who are interested in locating potential air emitters of 1,3-butadiene and making gross estimates of associated air emissions. Because of the generally limited data availability on potential sources of 1,3-butadiene, the emissions information summarized in this document does not and should not be assumed to represent emissions associated with any particular facility.

This section provides an overview of the contents of this document. It briefly outlines the nature, extent, and format of the material presented in the remaining sections of this report.

Section 3 provides a brief summary of the physical and chemical characteristics of 1,3-butadiene and an overview of its production, uses, and emission sources. This background section may be useful to someone who needs to develop a general perspective on the nature of 1,3-butadiene, how it is manufactured and consumed, and the potential sources of emissions that include production, use, and motor vehicles.

Section 4 focuses on the production of 1,3-butadiene and the associated air emissions. For each major production source category described in Section 4, an example process description and a flow diagram with potential emission points identified are given. Available emission estimates are used to calculate emission factor ranges that show the potential for 1,3-butadiene emissions before and after controls employed by industry. Also provided are estimates of annual emissions from equipment leaks. Individual companies that are reported in trade publications to produce 1,3-butadiene are named.

Section 5 describes major source categories that use 1,3-butadiene, primarily in the manufacture of synthetic elastomers. For each major production process, a description(s) of the process is given along with a process flow diagram(s). Potential emission points are identified on the diagrams and emission factor ranges are presented as estimates are available. Ranges of annual emissions due to equipment leaks are also given. Individual companies using 1,3-butadiene as a feedstock are reported.

Section 6 provides a brief summary on butadiene emissions from mobile sources. Section 7 summarizes the source categories, termed miscellaneous sources, that use smaller quantities of 1,3-butadiene. It also addresses emissions from indirect sources such as emissions from wastewater treatment of butadiene-containing wastewater and from other potential sources that are not clearly users or indirect sources as an "other" category. Limited information on these is available; therefore, varying levels of detail on the processes, emissions, and controls are presented. Locations of facilities for each source category as identified in the literature are provided.

The final section, Section 8, summarizes available procedures for source sampling and analysis of 1,3-butadiene. This section provides an overview of applicable sampling procedures, citing references for those interested in conducting source tests. Although a NIOSH sampling and analytical procedure is described, EPA has not yet developed a standard test method; thus, no EPA endorsement of this method is given or implied.

Appendix A presents the procedure for the derivation of 1,3-butadiene equipment leak emission estimates associated with the production processes presented in Sections 4, 5, and 7. Calculations for pump seals and pressure relief valves appear as examples of these derivations.

Appendix B provides facility specific data taken from Section 114 responses upon which the process vent and secondary source emission factors in Sections 4, 5, and 7 are based. Each facility has been assigned a letter code to prevent disclosure of their identity. In general, the equipment leak emissions shown have been calculated by applying average CMA emission factors to the equipment component counts from the Section 114 responses. The exceptions are butadiene producers and miscellaneous users. For producers, equipment counts were summarized by CMA for nine of the eleven facilities and the resulting emissions are presented as the most recent data. For the miscellaneous users, estimates based on SOCMI factors have been shown because equipment count data were not readily available to use with the average CMA emission factors. These had been calculated in earlier work done by EPA.

This document does not contain any discussion of health or other environmental effects of 1,3-butadiene, nor does it include any discussion of ambient air levels.

Comments on the contents or usefulness of this document are welcomed, as is any information on process descriptions, operating practices, control measures, and emissions information that would enable EPA to improve its contents. All comments should be sent to:

Chief, Pollutant Characterization Section (MD-15)
Noncriteria Pollutant Programs Branch
U. S. Environmental Protection Agency
Research Triangle Park, North Carolina 27711

SECTION 3
BACKGROUND

NATURE OF POLLUTANT

Butadiene is a colorless, flammable gas with a pungent, aromatic odor. It has a boiling point between -4 and -5°C. Table 1 summarizes butadiene's chemical and physical properties. Although butadiene is insoluble in water, it is slightly soluble in methanol and ethanol, and readily soluble at room temperature in common organic solvents such as benzene and ether.[1,2,3] It forms azeotropes with ammonia, methylamine, acetaldehyde, n-butene, and 2-butene.[2]

Butadiene is a highly versatile raw material that is used commercially in a variety of reactions. These include:

- Diels-Alder reactions with dienophiles to form a six-membered ring compound with a 2,3 double bond,
- conversion to cyclic or open chain dimers and trimers,
- telomerization with active hydrogen compounds,
- addition reactions with electrophilic and free radical compounds,
- oxidation reactions,
- substitution reactions, and
- polymerization.

Polymerization, with additions occurring at both the 1,2 and the 1,4 positions, are the basis for synthetic elastomer production, the major use of butadiene.[4]

Because of its reactivity, butadiene is estimated to have a short atmospheric lifetime on the order of four hours, where atmospheric lifetime is defined as the time required for the concentration to decay to 1/e (37 percent) of its original value.[5] The actual lifetime depends upon the

TABLE 1. PHYSICAL AND CHEMICAL PROPERTIES OF 1,3-BUTADIENE[2,3]

Property	Value
Structural Formula: C_4H_6, CH_2:CHCH:CH_2	
Synonyms: biethylene, bivinyl, butadiene, butadiene monomer divinyl, erythrene, methylallene, pyrrolylene, vinyl ethylene	
CAS Registry Number: 106-99-0	
Molecular Weight	54.09
Melting Point, °C	-108.91
Boiling Point, °C	-4.41
Partition Coefficient (log P, octanol/water)	1.99
Density at 20°C, g/cm^3	0.6211
Vapor Density	1.87
Critical Density, g/cm^3	0.245
Critical Temperature, °C	152
Critical Pressure, MPa (psi)	4.32 (626)
Critical Volume, mL/mol	221
Vapor Pressure, atm:	
15.3°C	2.0
47.0°C	5.0
Flash Point, °C	-105
Heat of Vaporization, J/g (cal/g):	
25°C	389 (93)
bp	418 (100)
Heat of Fusion, J/g (cal/g)	147.6 (35.28)

TABLE 1. (Continued)

Property	Value
Heat of Formation at 25^{o}C, kJ/mol (kcal/mol):	
Gas	110.2 (26.33)
Liquid	88.7 (21.21)
Free Energy of Formation at 25^{o}C, kJ/mol (kcal/mol):	
Gas	150.7 (36.01)
Explosive Limits, vol % butadiene in air:	
Lower	2.0
Upper	11.5
Solubility in Water at 20^{o}C, mg/L	735

conditions at the time of release. The primary removal mechanisms are through chemical reactions with hydroxyl radicals and ozone.[5] Therefore, factors influencing butadiene's atmospheric lifetime--time of day, sunlight intensity, temperature, etc.--also include those affecting the availability of hydroxyl radicals and ozone.

OVERVIEW OF PRODUCTION, USE, AND EMISSIONS

1,3-Butadiene production in the United States may be accomplished through either of two processes: recovery of butadiene from a mixed C_4 hydrocarbon stream generated during ethylene production or through oxidative dehydrogenation of n-butenes. Almost all, 1.36 million megagrams (3.00 billion pounds) in 1987,[4] results from recovery of butadiene as a by-product of ethylene generation. Of the 11 producers, nine are located in Texas, two in Louisiana. The majority of these producers generates the feedstock at the same location as butadiene production.[6]

Eighty-two percent of butadiene is used in synthetic elastomer production, 45 percent of which is dedicated to styrene-butadiene copolymer; 22 percent to polybutadiene; and 15 percent to neoprene, acrylonitrile-butadiene-styrene resin, and nitrile rubber. A second major use of butadiene, 12 percent, is in adiponitrile production, the raw material for nylon 6,6 production. The remaining 6 percent is divided between exports and miscellaneous uses.[4] Figure 1 illustrates these uses and the subsequent consumer endproducts.[4,7-11]

Overall, the demand for butadiene is projected to increase from 1.71 million megagrams (3.78 billion pounds) in 1987, of which 27 percent was supplied from imports, to 1.76 million megagrams (3.88 billion pounds) in 1992. Although the decrease in demand by the styrene-butadiene copolymer and polybutadiene industries for use in tire manufacturing is expected to continue, the specialty uses of butadiene should continue to grow.[4]

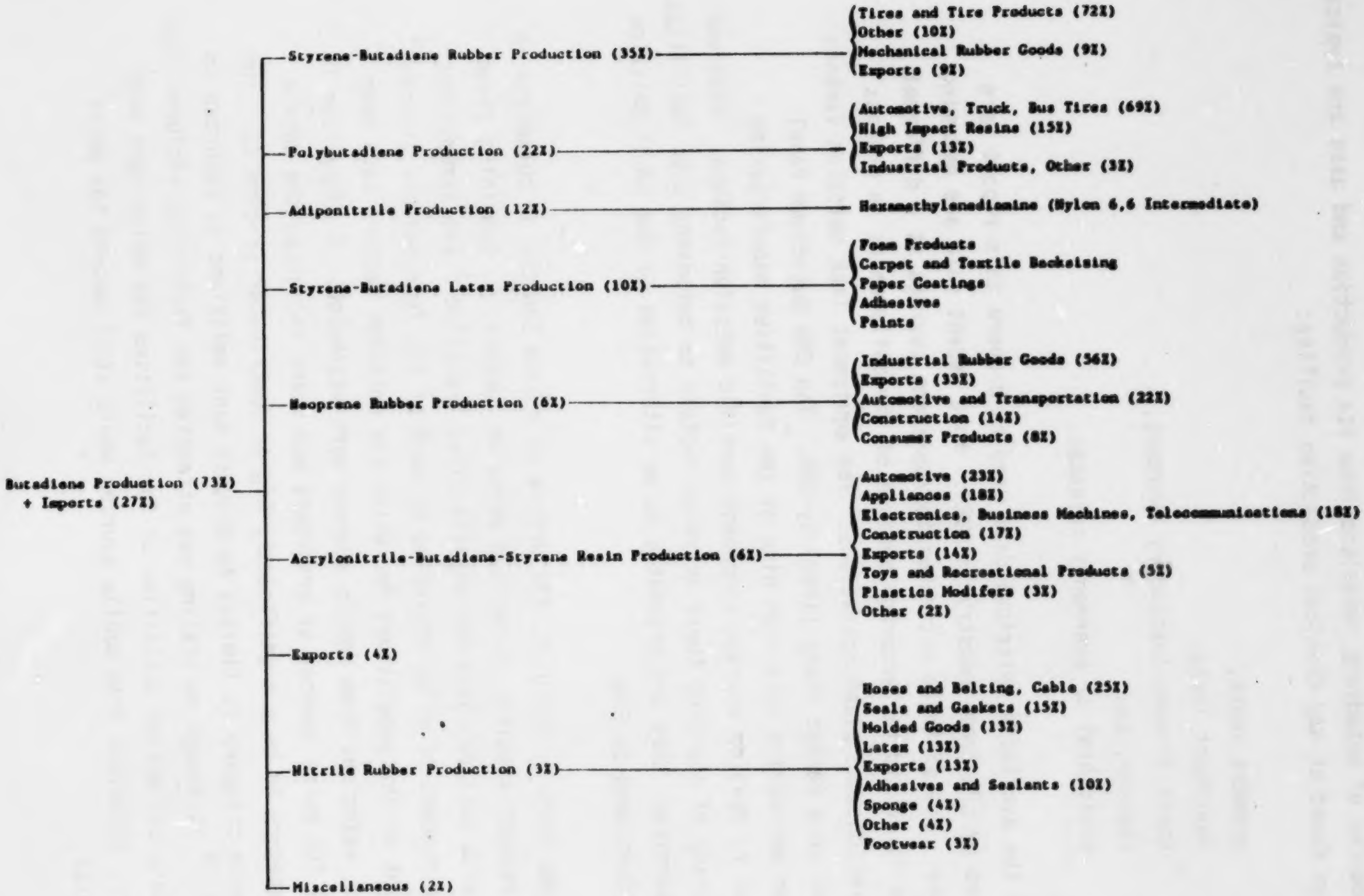
Butadiene Production (73%)
+ Imports (27%)
Styrene-Butadiene Rubber Production (35%)
Tires and Tire Products (72%)
Other (10%)
Mechanical Rubber Goods (9%)
Exports (9%)
Polybutadiene Production (22%)
Automotive, Truck, Bus Tires (69%)
High Impact Resins (15%)
Exports (13%)
Industrial Products, Other (3%)
Adiponitrile Production (12%)
Hexamethylenediamine (Nylon 6,6 Intermediate)
Styrene-Butadiene Latex Production (10%)
Foam Products
Carpet and Textile Backsizing
Paper Coatings
Adhesives
Paints
Neoprene Rubber Production (6%)
Industrial Rubber Goods (56%)
Exports (33%)
Automotive and Transportation (22%)
Construction (14%)
Consumer Products (8%)
Acrylonitrile-Butadiene-Styrene Resin Production (6%)
Automotive (23%)
Appliances (18%)
Electronics, Business Machines, Telecommunications (18%)
Construction (17%)
Exports (14%)
Toys and Recreational Products (5%)
Plastics Modifers (3%)
Other (2%)
Exports (4%)
Nitrile Rubber Production (3%)
Hoses and Belting, Cable (25%)
Seals and Gaskets (15%)
Molded Goods (13%)
Latex (13%)
Exports (13%)
Adhesives and Sealants (10%)
Sponge (4%)
Other (4%)
Footwear (3%)
Miscellaneous (2%)

Figure 1. Chemical Production and Use Tree for 1,3-Butadiene

Sources of butadiene emissions from its production and uses are typical of those found at any chemical production facility:

- process vents,
- equipment leaks,
- waste streams (secondary sources),
- storage, and
- accidental or emergency releases.

Much of the available emissions data used to prepare this report were collected by EPA from industry in 1984. More recent data are becoming available. Use of these estimates to represent sources at a different location is of limited accuracy because of the differences in process configurations and plant operations. The equipment leak emission factors are based on a recent study (1989) by CMA. The CMA Butadiene Panel collected monitoring data from nine of the facilities manufacturing butadiene to develop average component-specific emission factors. Although the accuracy of applying these emission factors to butadiene user facilities is undetermined, they are presented as an alternative to the SOCMI emission factors developed by EPA.

Recent work by the U. S. EPA Office of Mobile Sources on butadiene in vehicle exhaust resulted in revised emission factors.[12] Combining these factors with national data for vehicle miles travelled[13] and assumptions about the numbers of miles travelled by each of the four vehicle classes[14] (97 percent of the population) for which the emission factors have been developed, emissions from mobile sources were estimated. A comparison to the total for point sources at producers and users indicates the mobile source category to be a significantly higher contributor (Figure 2). The point source category is limited to process vent emissions as reported in 1984.[6,15-19] Although no scaling was attempted for facilities excluded from the EPA data collection activities or for facilities for which data were incomplete, emissions from mobile sources would still exceed the point source total.

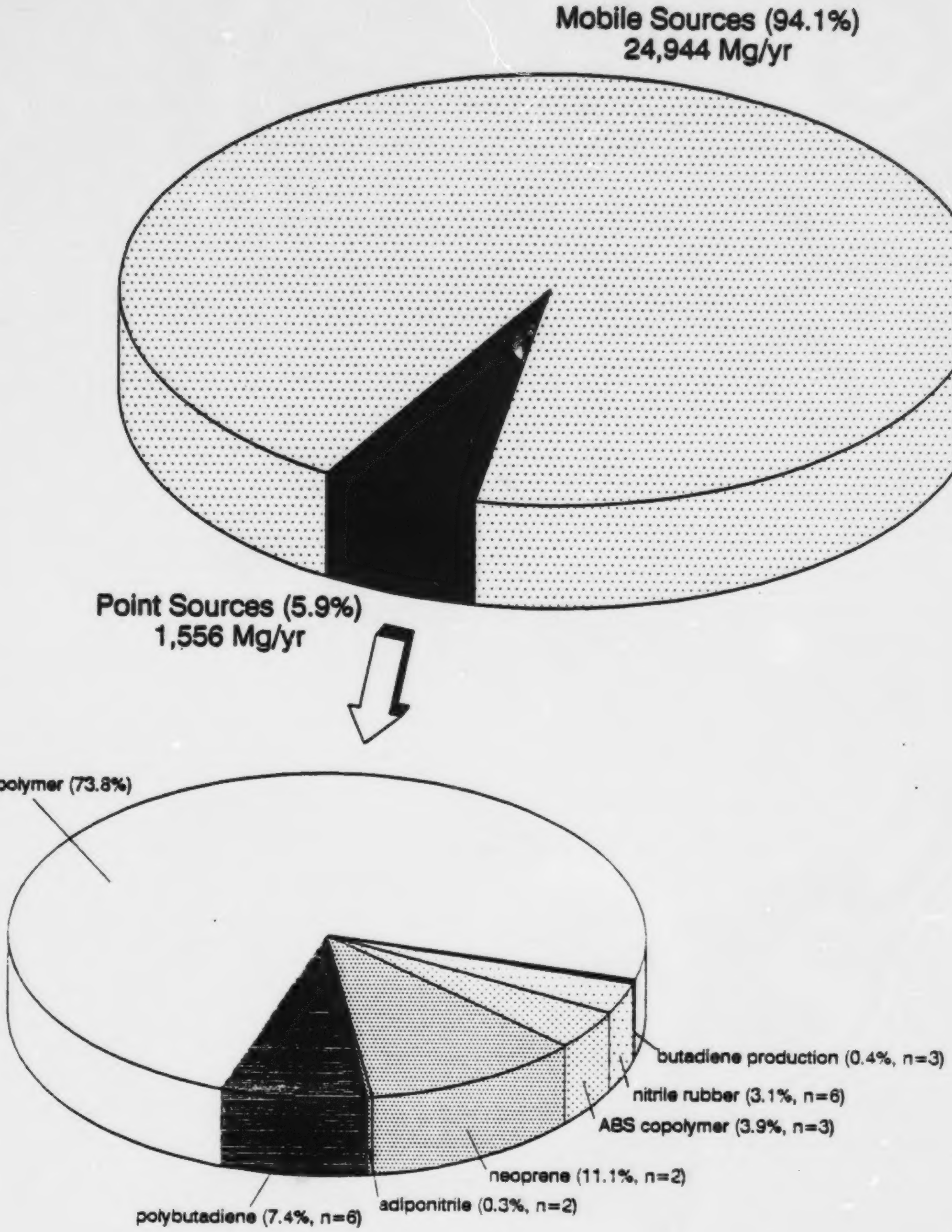

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Figure 2. Relative Contributions to Butadiene Emissions by Mobile and Point Source Categories

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17. Memorandum from K.Q. Kuhn and R.C. Burt, Radian Corporation, to the Butadiene Source Category Concurrence File, December 12, 1986. Estimates of 1,3-Butadiene Emissions from Miscellaneous Sources and Emissions Reductions Achievable with Candidate NESHAP Controls.

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19. Memorandum from R. Burt and R. Howle, Radian Corporation to L.B. Evans, EPA/Chemicals and Petroleum Branch, January 29, 1986. Estimates of Acrylonitrile, Butadiene, and Other VOC Emissions and Controls for ABS and NBR Facilities.

SECTION 4
EMISSIONS FROM BUTADIENE PRODUCTION

Butadiene emissions may occur during butadiene production and use, as well as during other chemical manufacturing processes that yield butadiene as a by-product. Emissions may also be generated by mobile sources or from materials containing butadiene. This section discusses emissions from sources associated with butadiene production. Butadiene emissions from other sources will be discussed in subsequent sections.

The information presented in this section includes identification of producers and descriptions of typical production processes. Process flow diagrams are given as appropriate with streams and vents labeled to correspond to the discussion in the text. Estimates of the associated butadiene emissions are provided in the form of emission factors when data were available to calculate them. Any known emission control practices are also discussed. Much of the process vent and secondary source emissions data were taken from a summary memo of facility-reported information that is based on responses to EPA's Section 114 (Clean Air Act) requests in 1984.[1] In many cases, these responses were incomplete. EPA is also in the process of collecting additional information under Section 114 as a part of a NESHAP development project. Interested readers should therefore contact specific facilities directly to determine the process in use, production volume, and control techniques in place before applying any of the emission factors presented in this document. This document will be reviewed as to the need to provide the newer data once it becomes available.

The equipment leak emission factors given in this section were calculated from producer screening data collected by CMA in 1988. The study is briefly described and results presented both in terms of average component-specific emissions factors and as annual emissions.

BUTADIENE PRODUCTION

The 1,3-isomer of butadiene, the only commercially significant isomer, is a high-volume intermediate organic chemical used to produce various types of rubber, resins, and plastics. Butadiene is produced by two different processes in the United States. One process involves the recovery of butadiene from a mixed C_4 hydrocarbon stream generated during ethylene production. The other is the oxidative dehydrogenation of n-butenes to produce butadiene.

Eleven facilities currently produce finished butadiene in the United States;[2] these are listed in Table 2. All of these recover butadiene from a mixed C_4 stream. The mixed C_4 streams feeding the recovery units are produced at olefins units co-located with the recovery units at these facilities, with the exception of one facility that receives its feedstock from an unidentified source. This facility also produces butadiene using the oxidative dehydrogenation of n-butenes process; quantities produced by this process depend on the market conditions.[1]

Process Descriptions

Recovery of Butadiene from a Mixed C_4 Stream--

This process consists of two distinct parts. First, a mixed C_4 stream containing butadiene is coproduced in an olefins plant during the cracking of large-molecule hydrocarbons to manufacture ethylene or other alkenes. The mixed C_4 stream is then routed to a recovery unit where the butadiene is separated.

The amount of butadiene produced during ethylene manufacture is dependent on both the type of hydrocarbon feedstock and the severity of the cracking operation. Typical butadiene yields from ethylene production based on various feedstocks are summarized in Table 3. Heavier feedstocks (naphthas and gas oils) produce much larger quantities of butadiene than the lighter feedstocks.

A generalized block flow diagram of an olefins unit producing a mixed C_4 coproduct stream, excluding the ethylene separation process, is

TABLE 2. BUTADIENE PRODUCTION FACILITIES[2]

Company	Location	Capacity (Mg/yr) in 1988	Production Process
Amoco Chemicals Company	Chocolate Bayou, TX	82,000	Recovery[a]
Cain Chemical	Chocolate Bayou, TX	61,000	Recovery
Cain Chemical	Corpus Christi, TX	95,000	Recovery
Exxon Chemicals Company	Baton Rouge, LA	141,000	Recovery
Exxon Chemicals Company	Baytown, TX	109,000	Recovery
Lyondell Petrochemical Company	Channelview, TX	205,000	Recovery
Mobil Chemical Company	Beaumont, TX	27,000	Recovery
Shell Chemical Company	Deer Park, TX	114,000	Recovery
Shell Chemical Company	Norco, LA	227,000	Recovery
Texas Chemical Company	Port Neches, TX	273,000	Recovery
Texas Petrochemicals Corporation	Houston, TX	364,000	Recovery (50%), Dehydrogenation[b] (50%)

[a] "Recovery" means butadiene as a coproduct in ethylene production is recovered from the mixed C_4 stream.

[b] Butadiene is produced from the dehydrogenation of n-butenes.

TABLE 3. BUTADIENE YIELDS FROM RECOVERY USING A MIXED C_4 STREAM PRODUCED FROM VARIOUS FEEDSTOCKS[a,b]

Feedstock	Yield Ratio (kg/100 kg)[c]
Ethane	1.0 - 2.0
Refinery offgas	5.0
Propane	5.0 - 8.5
n-Butane	7.0 - 8.5
Naphthas	13.0 - 18.0
Gas oils	17.6 - 24.7

[a] Refer to Figure 3 for a process diagram of mixed C_4 production olefins unit. Refer to Figure 3 for a diagram of a butadiene recovery process.

[b] Reference 1.

[c] Kilograms of butadiene per 100 kilograms of ethylene produced.

shown in Figure 3. In olefins production, a steam cracking furnace is used to crack the hydrocarbon feedstock (Step 1). The heavy hydrocarbons are broken into two or more fragments, forming a stream of mixed hydrocarbons. The concentration of butadiene in this mixed hydrocarbon stream varies with the type of feedstock. The flue gas from the cracking furnace is vented to the atmosphere (Vent A).

After the cracking step, the mixed hydrocarbon stream is cooled (Step 2) and, if naphtha or gas oils were the initial feedstock, the stream is sent to a gasoline fractionator (Step 3). The fractionator is used to recover heavy hydrocarbons (C_5 and higher). For some olefins units the quenching step shown occurs after gasoline fractionation. The mixed stream is then compressed (Step 4) prior to removal of acid gas (hydrogen sulfide) (Step 5) and carbon monoxide. Acid removal usually involves a caustic wash step. The mixed hydrocarbon stream then goes through additional refining steps (Step 6), where it is separated from olefins (C_3 and lower).

The composition of a typical C_4 coproduct stream from an ethylene plant using naphtha feedstocks is shown in Table 4. The mixed C_4 stream may be sent directly to butadiene recovery at the same plant. Olefins plants that do not produce finished butadiene use the by-product mixed C_4 streams in the following ways: (1) recover the crude butadiene from the stream and sell it to a butadiene producer, (2) recirculate the stream into the front of the ethylene process, and/or (3) use the stream to fuel the equipment (e.g., furnaces) in the ethylene process.

The second part of this butadiene production process involves recovering the butadiene from the mixed C_4 stream. A generalized block flow diagram of a butadiene recovery unit is shown in Figure 4. The mixed C_4 stream is fed from pressurized storage tanks into a hydrogen reactor along with hydrogen (Step 1) to convert some of the unsaturated hydrocarbons such as acetylene to olefins. The product C_4 stream from the hydrogenator is combined with a solvent (typically furfural) and fed into an extractive distillation operation (Step 2). In this operation, most of the butanes and butenes are separated from butadiene, which is absorbed in the solvent along

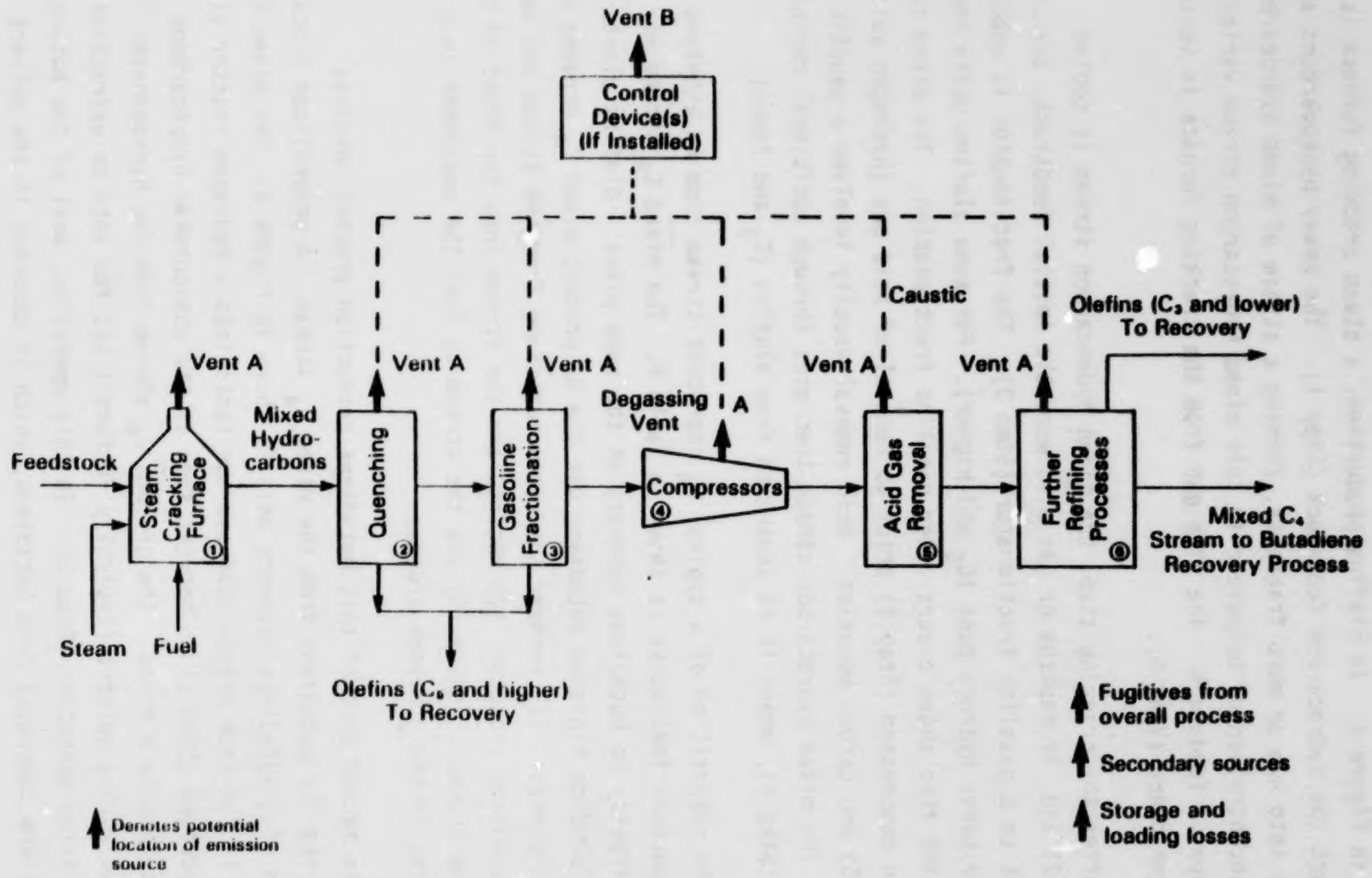
Vent B
Control Device(s) (If Installed)
Caustic
Olefins (C_3 and lower) To Recovery
Vent A
Vent A
Vent A
Degassing Vent
A
Vent A
Vent A
Feedstock
Steam Cracking Furnace ①
Mixed Hydro-carbons
Quenching ②
Gasoline Fractionation ③
Compressors ④
Acid Gas Removal ⑤
Further Refining Processes ⑥
Mixed C_4 Stream to Butadiene Recovery Process
Steam
Fuel
Olefins (C_6 and higher) To Recovery
Fugitives from overall process
Secondary sources
Storage and loading losses
Denotes potential location of emission source

Figure 3. Process Diagram for Production of a Mixed C_4 Stream Containing Butadiene

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TABLE 4. TYPICAL COMPOSITION OF MIXED C_4 STREAM FORMED FROM NAPHTHA FEEDSTOCK USED TO PRODUCE ETHYLENE[a,b]

Component	Molecular Formula	Composition (wt. %)
n-Butane	C_4H_{10}	6.8
Isobutane	C_4H_{10}	1.6
Isobutene	C_4H_8	29.0
1-Butene	C_4H_8	9.6
trans-2-butene	C_4H_8	7.5
cis-2-butene	C_4H_8	4.7
1,3-Butadiene	C_4H_6	39.3
1,2-Butadiene	C_4H_6	0.08
Propadiene	C_4H_4	0.53
Methyl acetylene	C_4H_4	0.65
Ethyl acetylene	C_4H_6	0.05
Dimethyl acetylene	C_4H_6	0.08
Vinyl acetylene	C_4H_4	0.11
TOTAL		100.0

---

[a] Refer to Figure 3 for process diagram of mixed C_4 production.

[b] Reference 3.

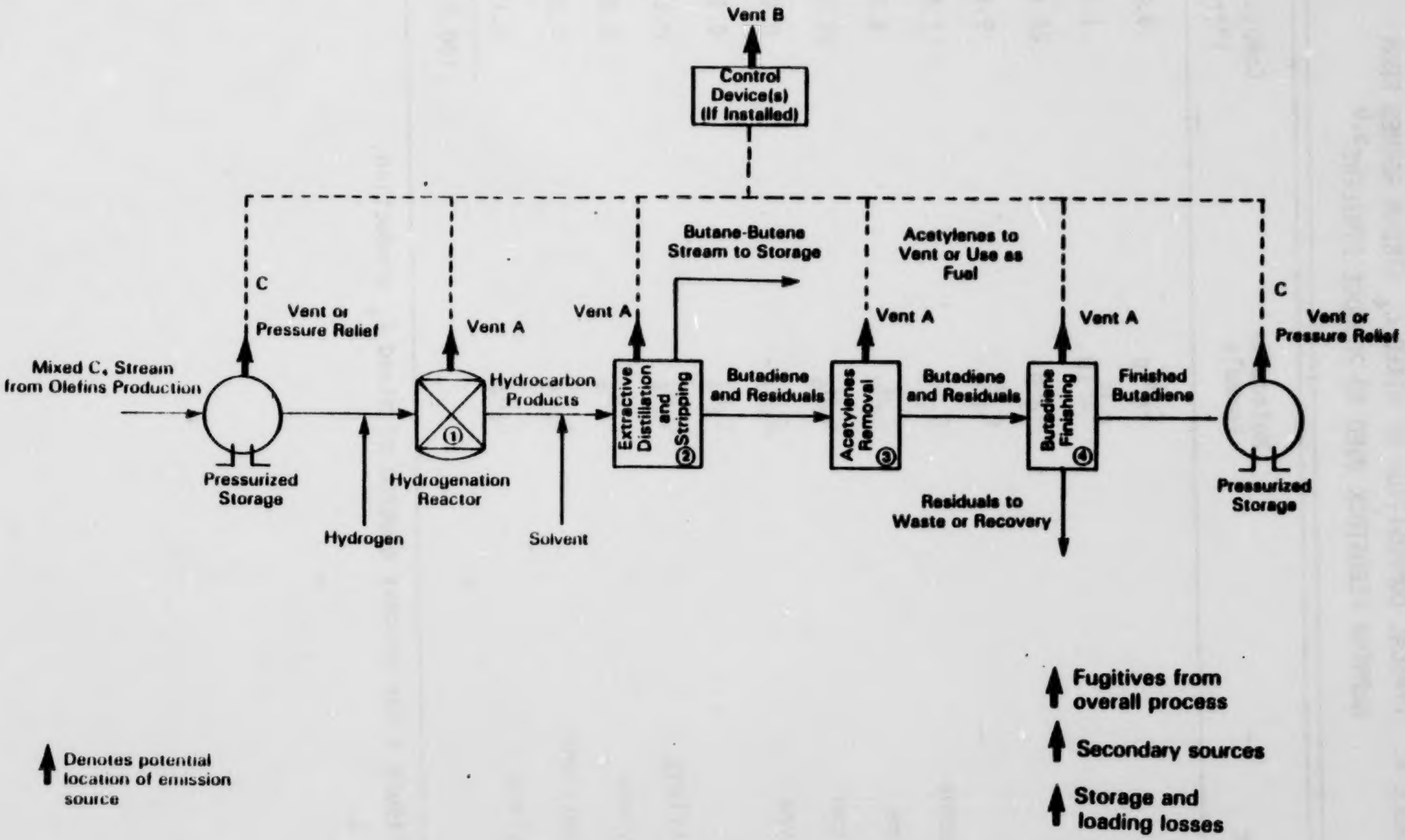
Vent B
Control Device(s) (If Installed)
C
Vent or Pressure Relief
Mixed C₄ Stream from Olefins Production
Pressurized Storage
Hydrogen
Vent A
Hydrogenation Reactor
①
Hydrocarbon Products
Solvent
Vent A
Extractive Distillation and Stripping
②
Butane-Butene Stream to Storage
Butadiene and Residuals
Vent A
Acetylenes Removal
③
Acetylenes to Vent or Use as Fuel
Butadiene and Residuals
Vent A
Butadiene Finishing
④
Residuals to Waste or Recovery
Finished Butadiene
C
Vent or Pressure Relief
Pressurized Storage
Denotes potential location of emission source
Fugitives from overall process
Secondary sources
Storage and loading losses

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Figure 4. Process Diagram for Butadiene Production by Recovery from a Mixed C_4 Stream

with residual impurities. A stripping operation is then used to separate the butadiene from the solvent.

The stream containing butadiene typically has a small amount of residuals. Some of these residuals are alkynes that were not converted to olefins in the hydrogenation reactor. These residuals are removed from the butadiene stream by distillation (Step 3) and are usually vented to an emission control device (Vent A). The bottom stream exiting the acetylenes removal operation contains butadiene and residuals such as polymer and 2-butene. The residuals are removed in the butadiene finishing operation (Step 4) and sent to a waste treatment system or recovery unit. The finished butadiene is then stored in pressurized tanks.

Oxidative Dehydrogenation of n-Butenes--

The oxidative dehydrogenation of n-butenes (1- and 2-butenes) proceeds through the following primary reaction:

$$\left.\begin{array}{c} CH_2 = CH - CH_2 - CH_3 \\ \text{(1-butene)} \\ \text{or} \\ CH_3 - CH = CH - CH_3 \\ \text{(2-butene)} \end{array}\right. + 1/2\ O_2 \longrightarrow CH_2 = CH - CH = CH_2 + H_2O$$

Between 1.1 and 1.3 kilograms of n-butenes are consumed per kilogram of butadiene formed.

A generalized block flow diagram of the butenes dehydrogenation process is shown in Figure 5. This has been developed from information given in Reference 1. A feed stream of n-butenes is combined with steam and air, preheated, and passed through a dehydrogenation reactor (Step 1). Air is used as a source of oxygen to remove hydrogen from the butenes feed. A typical composition of the product stream is shown in Table 5. The product stream is compressed after exiting the reactor (Step 2) and sent to a hydrocarbon absorption and stripping process (Step 3). During compression and absorption, vent streams containing nitrogen, excess oxygen, and

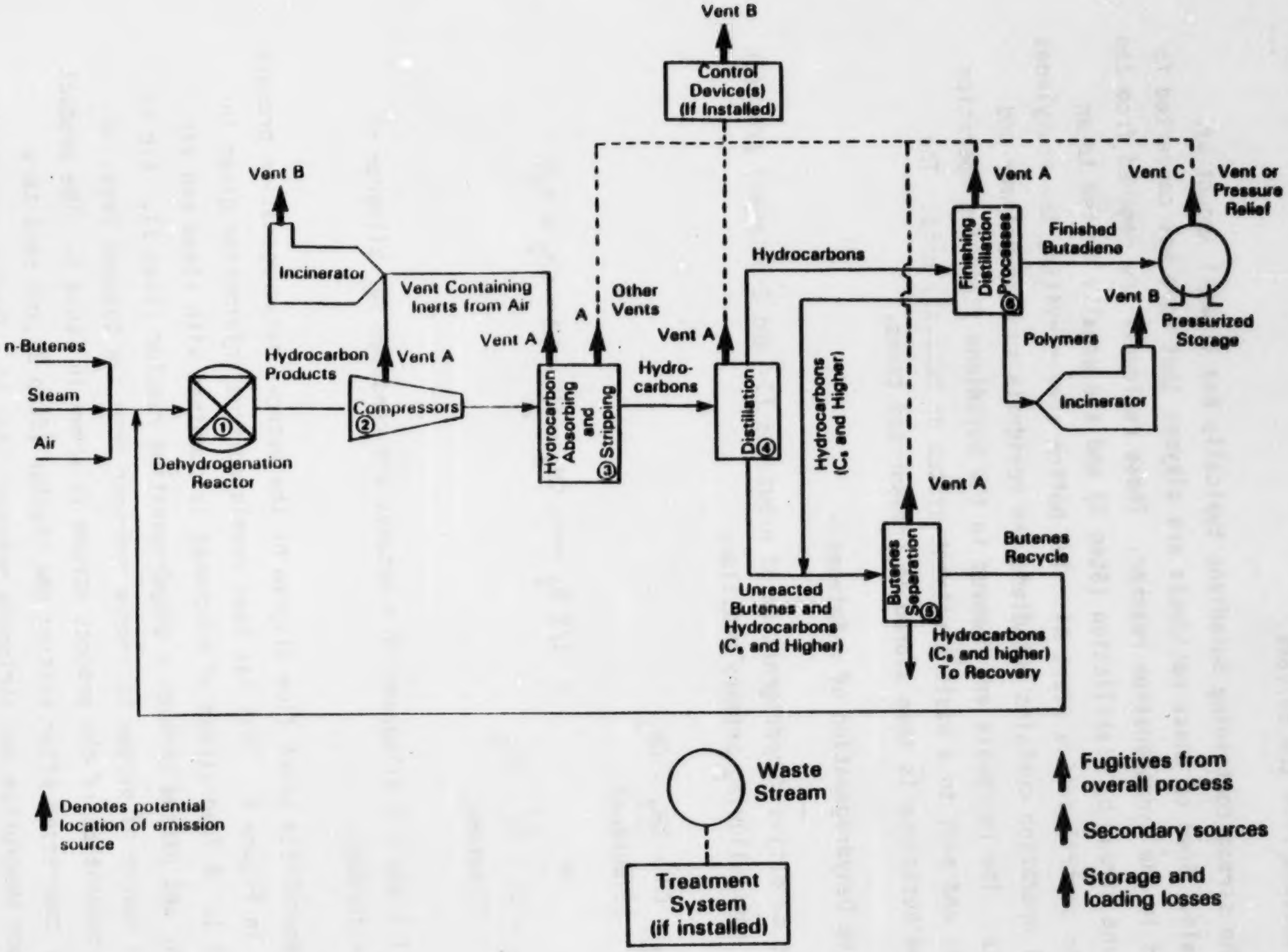
Vent B
Control Device(s) (If Installed)
Vent B
Incinerator
Vent Containing Inerts from Air
n-Butenes
Steam
Air
Dehydrogenation Reactor
①
Hydrocarbon Products
Vent A
Compressors
②
Vent A
A
Other Vents
Hydrocarbon Absorbing and Stripping
③
Hydro-carbons
Vent A
Distillation
④
Hydrocarbons
Hydrocarbons (C_5 and Higher)
Unreacted Butenes and Hydrocarbons (C_5 and Higher)
Vent A
Butenes Separation
⑤
Butenes Recycle
Hydrocarbons (C_5 and higher) To Recovery
Vent A
Finishing Distillation Processes
⑥
Finished Butadiene
Vent C
Vent or Pressure Relief
Pressurized Storage
Vent B
Polymers
Incinerator
Waste Stream
Treatment System (if installed)
Denotes potential location of emission source
Fugitives from overall process
Secondary sources
Storage and loading losses
098152OR

Figure 5. Process Diagram for Production of Butadiene by the Oxidative Dehydrogenation of Butene

TABLE 5. TYPICAL COMPOSITION OF n-BUTENES OXIDATIVE DEHYDROGENATION REACTOR PRODUCT STREAM[a,b]

Component	Molecular Formula	Composition (wt. %)
Oxygen	O_2	1.0
Nitrogen	N_2	15.8
Carbon Oxides	CO, CO_2	3.0
Water	H_2O	65.0
Methane	CH_4	0.1
C_2's		0.3
C_3's		0.4
n-Butane	C_4H_{10}	0.4
Isobutane	C_4H_{10}	0.6
Isobutene	C_4H_8	1.1
1-Butene	C_4H_8	1.9
trans-2-butene	C_4H_8	1.7
cis-2-butene	C_4H_8	1.4
1,3-Butadiene	C_4H_6	7.2
C_5's		0.1
1,2-Butadiene	C_4H_6	Trace
Propadiene	C_4H_4	Trace
Methyl acetylene	C_4H_4	Trace
Ethyl acetylene	C_4H_4	Trace
Dimethyl acetylene	C_4H_6	Trace
Vinyl acetylene	C_4H_4	Trace

[a] Refer to Figure 5 for process diagram of butadiene production by n-butenes oxidative dehydrogenation.

[b] Reference 4.

volatile organic compounds (VOCs) are routed to an incinerator. The overhead stream from the hydrocarbon stripping column (not shown in Figure 4) is routed to a light-ends column for further separation.

The C_4 and heavier compounds (labeled hydrocarbons) exiting the absorption/stripping process are fed to a distillation operation (Step 4) where butadiene is separated from the unreacted n-butenes. The n-butenes stream exiting the distillation operation also contains C_5 and heavier hydrocarbons. This stream is routed to a separation process (Step 5) where n-butenes are recovered and recycled to the dehydrogenation reactor.

The stream containing butadiene from the distillation process (Step 4) is routed to a finishing distillation process (Step 6). At this point, finished butadiene is separated from other hydrocarbons and sent to pressurized storage. A polymer waste stream generated during the finishing process is routed to an incinerator. The hydrocarbons are sent to butene separation process units.

Emissions

Regardless of the process used to produce butadiene, emissions of butadiene at a production facility may be of five general types: process vent discharges; equipment leaks; emissions from secondary sources (wastewater, liquid waste, or solid waste discharges); storage-related releases; and emergency or accidental releases. The letter A denotes process vents in Figures 3, 4, and 5, B represents emissions after a control device, and C indicates vents or pressure relief devices from storage vessels.

No information about emissions associated with storage or emergency/accidental releases is available. Storage vessel discharges may be assumed to be negligible because butadiene is stored in pressure vessels that have no breathing or working losses. Some losses during transfer of butadiene are possible, if the butadiene is not used on-site; these should also be low for safety reasons and to reduce product loss.

Emissions are presented in the form of emission factor ranges for process vents and secondary sources. Individual emission factors having units of kilograms of butadiene emitted per megagram of butadiene produced (kg/Mg) are first calculated for each facility by dividing facility-specific estimates by production, taken as 80 percent of capacity.[1] From these facility-specific emission factors, a range for each source is established. The values of n indicates the number of facilities included. Because facilities reported varying levels of controls, two sets of emission factor ranges were developed. One reflects actual facility emissions in which each facility may control all, some, or none of their sources. The second incorporates both emissions from existing uncontrolled sources and potential emissions from controlled sources if controls had not been in place.

Equipment leak emissions are based on equipment count data collected by CMA and average CMA emission factors. They are reported in units of megagrams of butadiene emitted per year (Mg/yr).

Facility-specific emission estimates and capacity data appear in Appendix B, Tables B-1 through B-4. These emission factor ranges and annual emissions should be used only as order-of-magnitude approximations, since differences in production processes, among other variables, may significantly influence actual emissions. The equivalents in English units, pounds butadiene emitted per ton produced (lbs/ton) and tons butadiene emitted per year (tons/yr), are given in parentheses below the metric values.

Process Vent Discharges--

Process vent discharges occur from reactor vessels, recovery columns, and other process vessels. They may occur continuously (from a continuous process) or intermittently (from a batch process). Some continuous processes also have intermittent VOC emissions during startup and shutdown, or during control device malfunction or process upsets.

The possible locations of these process vents are shown in Figures 3 through 5. The actual locations and butadiene content may vary depending on the particular facility design. In some cases, process vents are directed to other parts of the plant or to a gas recovery system for use as fuel, rather than discharged to the atmosphere.

Emissions data, including the use of control devices (six use flares, of which two also have gas recovery systems), were available for some facilities (see Appendix B). An emission factor range derived from these data is presented in Table 6. Also included in the table is an uncontrolled emission factor range to provide an indication of the extent to which controls are used. These were calculated using the emission reduction efficiencies listed in Table 7.

Both processes for olefins production and butadiene production via oxidative dehydrogenation are potential sources of emissions. However, the emissions data are limited to the olefins process at the two facilities. One of the facilities is reportedly controlling process vents on the oxidative dehydrogenation process at the hydrocarbon absorbing and stripping column and at the compressors (incinerator and flare) (see Figure 5).

Equipment Leaks--

Emissions from process equipment components occur when the liquid or gas process streams leak from the equipment. These components include: pump seals, process valves, compressors, safety relief valves (pressure relief devices), flanges, open-ended lines, and sampling connections.

The emission estimates shown in Table 6 are the results of a study conducted by CMA.[5] The study objective was to develop industry-specific emission factors to replace SOCMI emission factors[9] because they were thought to overestimate equipment leak emissions for butadiene producers. The study recommends, however, that screening data and correlation equations (also revised) be used to generate the most accurate estimates.

TABLE 6. SUMMARY OF EMISSION FACTORS FOR BUTADIENE PRODUCTION FACILITIES[1,5]

Emission Sources	Facility Emission Factors[a,b]		Uncontrolled Emission Factors[a]	
	Range	Mean	Range	Mean
Process Vents:				
C_4 stream production	---[c]	---	0.0027 kg/Mg	—
Recovery process	0.0034 - 0.0275 kg/Mg (n=3) (0.0068 - 0.0550)	0.0157 kg/Mg (0.0314)	0.0161 - 0.3436 kg/Mg (n=3) (0.0322 - 0.6872)	0.2326 kg/Mg (0.4652)
Equipment Leaks:				
Recovery process[d]	407 Mg/yr (n=9) (455)	—	---	---
Secondary Sources:				
Recovery process - wastewater	0.00034 - 2.2 kg/Mg (n=6) (0.00068 - 4.4)	0.468 kg/Mg (0.936)	---	---
Recovery process - solid waste	Negligible[e] (n=2)	—	---	---

[a] Assumes production capacity = 80 percent. Values are in units of kg butadiene emitted per Mg produced or, in the case of equipment leaks, Mg butadiene emitted per year. The numbers in parentheses are in units of pounds butadiene emitted per ton produced (lbs/ton) or tons emitted per year (tons/yr).

[b] Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

[c] "---" means no data available.

[d] Total numbers of components = 79,430: 60 percent flanges, 29 percent liquid valves, 8 percent gas valves, and 3 percent all others combined.

[e] Defined as 0.4988×10^{-6} kg/Mg.

TABLE 7. VOC EMISSION REDUCTION EFFICIENCIES OF CONTROL DEVICES USED TO ESTIMATE CURRENT BUTADIENE EMISSIONS

Control Device[a]	Reduction Efficiency (%)	Reference
Gas recovery (boiler)	99.9	6
Flare	98	7
Incinerator	98	8

[a] Devices reported by industry to control vent streams and secondary emissions. Possible placement of control devices are shown in Figures 3 through 5.

The Butadiene Panel of CMA designed their study to closely adhere to EPA protocols for generating unit-specific emission estimates as specified in the 1987 draft "Protocols for Generating Unit-Specific Emission Estimates for Equipment Leaks of VOC and VHAP." In addition to using the protocols, the Butadiene Panel sought EPA comments on the procedure before they began collecting data. Nine of the eleven finished butadiene producers in the United States participated in the study. The exceptions were the Shell facility in Norco, Louisiana, which was not in service and the Texas Petrochemical facility in Houston, Texas. Four facilities that produce only crude butadiene also contributed data: three Union Carbide plants in Seadrift, Texas; Taft, Louisiana; and Texas City, Texas; and Dow Chemical in Freeport, Texas. All produce butadiene by the recovery process. No estimate of equipment leak emissions from the oxidative dehydrogenation process was possible due to the lack of equipment component counts.

Based on facility data, the following ranges of butadiene concentrations through equipment components were established: 5-30 percent, 30-90 percent, and 70-100 percent. From the total numbers of each component in each range the weighted average percents were calculated. Approximately 20 percent of components were associated with butadiene streams having between 5-30 percent concentration, 47 percent with the 30-90 percent butadiene range, and 33 percent with the 90-100 percent butadiene range.

The screening data collected were similarly grouped into ranges of concentration (parts per million, ppm) based on the instrument readout and the butadiene concentration in the stream. Five ranges from 0-9 ppm to >9999 ppm were used. On calculating weighted average percents, about 76 percent of components fell in the 0-9 ppm range, and 19 percent in the 10-99 ppm range. Less than six percent were found to be greater than 100 ppm.

Table 8 summarizes the study results. In addition to average emission factors, average butadiene concentration in the stream through each type of component is shown. These average concentrations have been used to convert SOCMI factors from units of VOC emissions to butadiene emissions for

TABLE 8. AVERAGE BUTADIENE EMISSION FACTORS FOR PROCESS EQUIPMENT COMPONENT LEAKS[5]

Equipment Component (Emission Source)	Average Emission Factor[a] (kg BD/hr/component)	Average Butadiene Concentration (%)	Reduction[b] (%)
Pumps - Liquid	0.02555 (0.05634)	64.1	19.3
Compressors	0.0000018 (0.000004)	27.9	99.9+
Flanges	0.000139 (0.000307)	61.0	72.5
Valves - Gas	0.000501 (0.001105)	60.2	85.1
Valves - Liquid[c]	0.001424 (0.003140)	59.7	66.3
Pressure Relief Devices "Safety Valves:	0.013590 (0.02996)	56.7	76.9
Sampling Point[d]	-	-	-
Open-ended Lines	0.000054 (0.000120)	67.9	95.2

---

[a] Number in parentheses is in units of lbs/hr/component.

[b] Calculated as $\left[1- \frac{\text{CMA emission factor}}{\text{SOCMI emission factor}}\right] \times 100$

[c] Liquid refers to light liquid and is defined as a petroleum liquid with a vapor pressure greater than the vapor pressure of kerosene.

[d] Sampling points were considered to be a subset of open-ended lines; therefore, data were incorporated in the open-ended line average emission factor.

purposes of comparison to the new emission factors. The results of this comparison are also given in Table 8.

In addition to compiling the data from all facilities, the study analyzed the data on a plant-specific level. Table 9 provides the variability among the plants by component type determined from this analysis.

The emissions shown in Table 8 include the reduction achieved by the various controls that the 13 facilities have in place. The Butadiene Panel distributed a survey to identify and evaluate practices in the plants that would contribute to emissions reduction. Of the six respondents, all stated they monitor fugitive emissions using a combination of visual observation and automatic audible alarm for specific equipment such as pumps and compressors. Three have routine leak inspection and maintenance programs. Two informally require immediate repair of leaks detected by the monitoring system. Five of the six plants reported combinations of visual inspections, pressure testing, VOC monitoring, use of double-sealed pumps, seals vented to a flare, bubble-testing flanges, tightness testing of valves, use of special packing material, closed loop sampling points, and plugging of all open-ended lines. No estimate of the emission reduction achieved by these practices was determined.

In the absence of specific information that relates controls in use to reduction achieved, previously developed control efficiencies[10] are presented in Table 10 to provide an indication of typical reductions achieved. To apply these efficiencies and determine emissions after controls, an estimate of uncontrolled emissions would be multiplied by [1-(efficiency/100)]. An example that uses SOCMI emission factors to estimate uncontrolled emissions is shown in Appendix A.

Secondary Emissions--

Secondary emissions occur during the treatment and disposal of wastewater, other liquid waste and solid waste. Few emissions estimates are

TABLE 9. VARIABILITY IN FACILITY-SPECIFIC EMISSION FACTORS FOR EQUIPMENT LEAKS[a]

Equipment Component	Relative Standard Deviation (%)
Pumps - Liquid	96.0 (n=13)
Compressors	137.4 (n=3)
Flanges	91.4 (n=13)
Valves - gas	84.3 (n=13)
Valves - liquid	45.2 (n=13)
Pressure Relief Devices	226.6 (n=10)
Open-ended lines	117.8 (n=6)
Sample points	102.1 (n=4)

[a] Reference 5, pp. 5-30, 5-35, 5-41, 5-47, 5-53, 5-58, 5-63, 5-68.

TABLE 10. CONTROL TECHNIQUES AND EFFICIENCIES APPLICABLE TO EQUIPMENT LEAK EMISSIONS

Equipment Component (Emission Source)	Control Technique	Percent Reduction in Butadiene Emissions[a]
Pump Seals		
Packed and Mechanical	**Monthly LDAR[b]**	**61**
	Quarterly LDAR	**32**
	Semiannual LDAR	**0**
	Annual LDAR	**0**
Double Mechanical	**N/A[d]**	**--**
Compressors	**Vent Degassing Reservoir to Combustion Device**	**100**
Flanges	**None available**	**0**
Valves		
Gas	Monthly LDAR	73
	Quarterly LDAR	64
	Semiannual LDAR	50
	Annual LDAR	24
Liquid	Monthly LDAR	59
	Quarterly LDAR	44
	Semiannual LDAR	22
	Annual LDAR	0
Pressure Relief Devices		
Gas	Quarterly LDAR	44
	Rupture Disk	100
Liquid	N/A	--

TABLE 10. (Continued)

Equipment Component (Emission Source)	Control Technique	Percent Reduction in Butadiene Emissions[a]
Sample Connections	Closed-purge Sampling	100
Open-ended Lines	Caps on Open Ends	100

[a] Percent reduction in butadiene emissions based on the SOCMI VOC emission factors and data from Reference 10. Butadiene emissions were assumed to be reduced by the same percentage as VOC emissions. If Reference 10 indicated a negative reduction for a control technique, zero was used.

[b] LDAR = Leak detection and repair.

[c] Assumes the seal barrier fluid is maintained at a pressure above the pump stuffing box pressure and the system is equipped with a sensor that detects failure of the seal and/or barrier fluid system.

[d] N/A = Not applicable. There are no VOC emissions from this component.

available and most of these data pertain to wastewater from the butadiene recovery process. Table 6 summarizes emission factors derived from estimated wastewater and solid waste emissions (Appendix B). None are available for the olefins process, the oxidative hydrogenation process, or for any liquid waste other than wastewater. The types of waste streams generating butadiene emissions include cooling water, wash water, solvent recovery wastewater, process unit wastewater, and waste polymer.

Due to its low solubility in water and its volatility, butadiene in a waste stream is assumed to completely volatilize, unless the vapor is routed to a control device. Some facilities use such emission control systems; others do not. Available information on the facility control status and handling of the waste streams is summarized in Appendix B.

REFERENCES FOR SECTION 4

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SECTION 5
EMISSIONS FROM MAJOR USES OF BUTADIENE

Emissions from industrial processes using butadiene as a raw material are discussed in this section. Butadiene has six primary commercial uses as illustrated in the chemical use tree in Figure 1 (see Section 3). These are the production of styrene-butadiene (SB) copolymer, polybutadiene, adiponitrile, neoprene, acrylonitrile-butadiene-styrene (ABS) copolymer, and nitrile elastomer. This section will be divided into subsections, one for each major use. Each subsection will provide a general discussion of the production process, estimates of the associated butadiene emissions, and a description of any existing emission control practices. These are primarily based on summary memoranda of Section 114 questionnaires, National Institute for Occupational Safety and Health (NIOSH) survey reports, and various other reports as referenced, representing information gathered prior to 1986. The level of detail will vary according to the availability of information, particularly on emissions where data may be absent or incomplete. In view of these limitations, the reader is advised to contact the facilities for more complete and accurate information.

As with butadiene production sources, emission factor ranges (in units of kilograms butadiene emitted per megagram produced) are provided for process vents and secondary sources, based on annual emissions estimates (megagram per year). The same procedure described in Section 4 for calculating facility emission factors was followed to establish these ranges. Assumptions about production are provided in each subsection.

Equipment leak emissions are presented as annual emissions that were derived using the procedure in Appendix A and the CMA emission factors presented in Section 4. Although developed for butadiene producers, these emission factors were assumed to better represent practices of the user industries because all involve butadiene handling. Two alternative methods would be to collect screening data and use correlation equations established in the CMA work and to apply SOCMI emission factors, weighted for the percent butadiene in the stream. The equipment leak emissions estimates generally represent uncontrolled emissions because no specific information on controls was available from the summary memoranda. A discussion of control practices is provided to supplement these whenever this had been described by the facilities.

The emission factors and annual emission values should be used only as estimates since facilities did not always provide complete information and source characteristics cannot be assumed to be the same from location to location. The number of facilities included in establishing the range is indicated in parentheses; the individual values are reported in Appendix B.

Company identification and corresponding facility locations for the various production process are also given in each subsection. The production capacities supplied are, in most cases, taken from more recent (1985-1988) references.

STYRENE-BUTADIENE COPOLYMER PRODUCTION

Styrene-butadiene copolymers are composed of the monomer units butadiene and styrene. Depending upon the feed composition and extent of drying in the process, SB copolymers can be solid or an emulsion.

The copolymers of styrene and butadiene that contain over 45 percent butadiene have rubber-like properties. The copolymers become more plastic-like when the styrene content is increased above 45 percent.[1] Copolymers with more than 45 percent butadiene are sometimes referred to as styrene-butadiene rubber (SBR), while products with more styrene may be referred to as styrene-butadiene (SB) latex. No distinction will be made in the subsequent discussion because emissions data are not differentiated. The term elastomer will be used in a generic sense, meaning solid copolymer.

Styrene-butadiene latex is an elastomer emulsion. Styrene-butadiene rubber is also used as an emulsion. The emulsion process is the same process used for elastomers, except that it lacks the emulsion breaking (coagulation) and drying steps. The term latex will be used when referring to both SB and SBR emulsion.

Styrene-butadiene copolymers account for 45 percent of national butadiene consumption.[2] The majority of SB elastomer produced is used by the tire industry. The latex finds a wider variety of uses in industries such as textiles, paper, and adhesives manufacturing.

Process Description

Elastomer is manufactured by two processes: (1) the emulsion process, where monomer is dispersed in water, and (2) the solution process, where monomer is dissolved in a solvent. The emulsion process is the one more commonly used. Latex is similarly produced but is removed prior to the final processing that generates the solid copolymer.

A generalized block flow diagram of an elastomer and latex production process is shown in Figure 6. Stored butadiene and styrene monomers are first washed to remove any inhibitors of the polymerization reaction (Step 1). The scrubbed monomers are then fed into polymerization reactors (Step 2) along with the ingredients listed in Table 11. After the polymerization reaction has progressed to the desired extent, a polymer emulsion (latex) is removed from the reactors along with unreacted monomer (Step 3). Both styrene and butadiene are separated from the latex and recycled to the monomer feed tanks.

The unfinished latex may take one of two routes after monomer is removed. One route is for the latex to be blended into a homogenous emulsion (Step 4) and stored as finished latex. The other route involves a coagulation operation where the emulsion is broken (Step 5). This step is followed by washing and drying of the polymer into a solid form (Step 6).

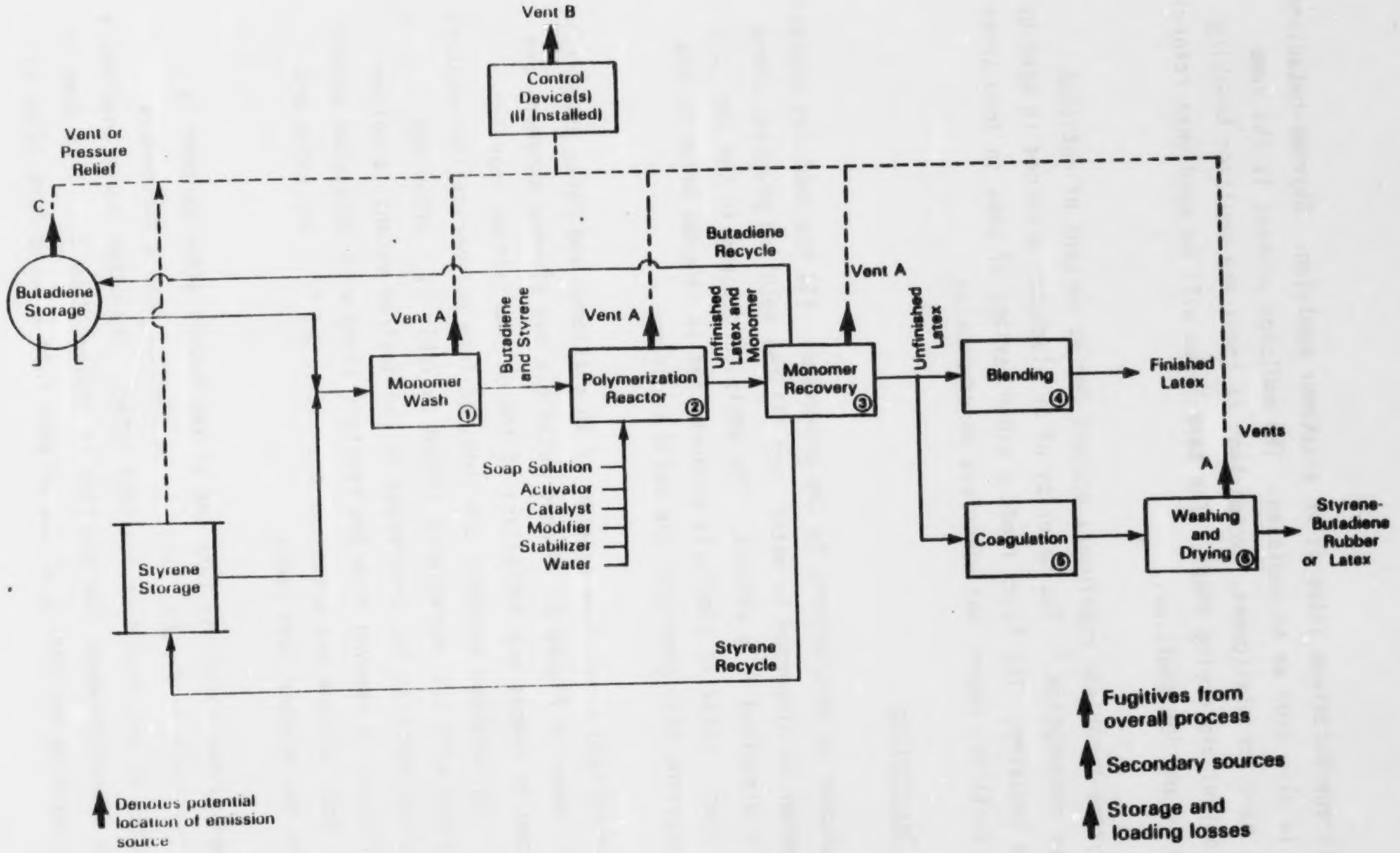
Vent B
Control Device(s) (If Installed)
Vent or Pressure Relief
C
Butadiene Storage
Butadiene Recycle
Vent A
Vent A
Vent A
Monomer Wash ①
Butadiene and Styrene
Polymerization Reactor ②
Unfinished Latex and Monomer
Monomer Recovery ③
Unfinished Latex
Blending ④
Finished Latex
Vents
A
Soap Solution
Activator
Catalyst
Modifier
Stabilizer
Water
Styrene Storage
Coagulation ⑤
Washing and Drying ⑥
Styrene-Butadiene Rubber or Latex
Styrene Recycle
Fugitives from overall process
Secondary sources
Storage and loading losses
Denotes potential location of emission source
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Figure 6. Process Diagram for Production of SB Copolymer

TABLE 11. TYPICAL RECIPE FOR EMULSION SBR[3]

Components	Weight Percent	Function
Butadiene	25.0	Monomer
Styrene	10.0	Monomer
d-Isopropyl Benzene Hydroperoxide	<.1	Catalyst
Ferrous Sulfate	<.1	Activator
Tert-Dodecyl Mercaptan	.1	Modifier
Potassium Pyrophosphate	.1	Buffer
Rosin Acid Soap	1.4	Emulsifier
Water	63.0	

Table 12 lists the known production facilities grouped by copolymer type. Since three different latexes may be produced--SBR, SB and styrene-butadiene-vinylpyridine--footnotes have been provided to indicate which ones each facility manufactures.

Emissions

The emission sources at an SB copolymer facility are typical of those common to chemical production facilities: process vent discharges, equipment leaks, wastewater, liquid waste or solid waste discharges (secondary emissions), storage-related releases, and accidental or emergency releases. Available emissions data are limited to emissions from process vents, equipment leaks and secondary emissions and appear in Tables B-5 through B-8 in Appendix B. In developing emission factors the facilities were assumed to be operating at 80 percent of their production capacity.[1]

As with butadiene production, butadiene used in elastomer production is usually stored in pressurized vessels vented to a flare, point C in Figure 6. Storage, therefore, results in low emissions. Two facilities, however, store butadiene-containing material in fixed roof storage tanks. Emissions are estimated to be low because of the low concentrations of butadiene (5 percent by weight or less). Losses during butadiene transfer and loading and resulting from accidental and emergency releases are currently unquantified.

Process Vent Emissions--

As seen from the vent locations in Figure 6, process vent discharges occur from reactor vessels, recovery columns, and other process vessels. They may occur continuously (from a continuous process) or intermittently (from a batch process). Some continuous processes have emissions during startup and shutdown or during a control device malfunction or process upset.

TABLE 12. STYRENE-BUTADIENE ELASTOMER AND LATEX PRODUCTION FACILITIES[4,5]

Company	Location	Capacity (Mg/yr) in 1987[a,b]
Elastomer		
Ameripol Synpol	Port Neches, TX	333,000
Copolymer Rubber	Baton Rouge, LA	125,000
Firestone	Lake Charles, LA	120,000
GenCorp	Odessa, TX	90,000
Goodyear	Houston, TX	305,000
Latex		
Ameripol Synpol	Port Neches, TX	5,000[c]
Dow Chemical	Dalton, GA	159,000[d]
Dow Chemical	Freeport, TX	
Dow Chemical	Gates Ferry, CT	
Dow Chemical	Midland, MI	
Dow Chemical	Pittsburgh, CA	
GenCorp	Mogadore, OH	62,000[e]
Goodyear	Akron, OH	3,000[c]
Goodyear	Calhoun, GA	45,000[e]
Goodyear	Houston, TX	26,000[f]
W. R. Grace	Owensboro, KY	4,500
Polysar	Monaca, PA	66,000[f]
Polysar	Chattanooga, TN	
Reichhold (DE)	Cheswold, DE	73,000
Reichhold (GA)	Kensington, GA	
Unocal	Charlotte, NC	46,000
Unocal	La Mirada, CA	

[a] Weight for elastomer is dry weight.

[b] Unless otherwise foonoted, latex values include production of both SB and SBR latexes.

[c] Facility coproduces SBR latex and styrene-butadiene-vinylpyridine latex.

[d] Facility only produces SB latex.

[e] Facility coproduces all three latexes.

[f] Facility only produces SBR latex.

[g] The Monaca facility only produces SB latex.

The potential locations of these process vents (Vent A) are shown in Figure 6. Although the actual locations and butadiene content may vary depending on the facility design, process vents are typically located on absorption columns used to recover butadiene. In some cases, process vents are directed to other parts of the plant, or to a gas recovery system for use as fuel, rather than discharged to the atmosphere.

The available emissions data are presented in Table 13 as emission factor ranges having units of kilograms butadiene emitted per megagram of product (kg/Mg). The English unit equivalents in pounds per ton (lbs/ton) are shown in parentheses. The value of n indicates the number of facilities included. Calculated as described in Section 4.0, the facility emission factor range reflects actual emissions and includes the various levels of control reported. The second emission factor range incorporates both emissions from existing uncontrolled sources and potential emissions from controlled sources with controls removed.

Although 20 facilities supplied emissions data (Table B-6), production capacities for two were not available; therefore, these two were omitted from the emission factor range development. Control devices in use include absorbers, boilers, flares, scrubbers, and pressure condensers. Emissions after controls (denoted Vent B) were calculated by applying appropriate reduction efficiencies. Standard control efficiencies from Table 7 were used to calculate controlled emissions unless alternate values were supplied by the companies and accompanied by quantitative documentation.

Equipment Leaks--

Emissions occur from process equipment components whenever the liquid or gas process streams leak from the equipment (identified in the diagram as point C). Butadiene emissions were estimated for the following equipment components: pump seals, process valves, compressors, safety relief valves (pressure devices), flanges, open-ended lines, and sampling connections. For each facility where the number of equipment components is known, uncontrolled emissions were estimated using emission factors previously

TABLE 13. SUMMARY OF EMISSION FACTORS FOR SB COPOLYMER PRODUCTION FACILITIES[1]

Emission Sources	Facility Emission Factors[a,b]		Uncontrolled Emission Factors[a]	
	Range	Mean	Range	Mean
Process Vents	0.00012 - 47.17 kg/Mg (n=18) (0.00024 - 94.34)	3.55 kg/Mg (7.10)	0.062 - 47.17 kg/Mg (n=18) (0.124 - 94.34)	7.10 kg/Mg (14.20)
Equipment Leaks	Not available	—	0.10 - 21.40 Mg/yr (n=19) (0.11 - 23.59)	6.60 Mg/yr (7.28)
Secondary Sources:				
Wastewater	0 - <5 kg/Mg[c] (n=18) (0 - <10)	0.15 kg/Mg (0.30)	---[d]	---
Other liquid waste	<0.01 kg/Mg (n=5) (<0.02)	<0.01 kg/Mg (<0.02)	---	---
Solid waste	0 - <0.01 kg/Mg[c] (n=11) (0 - <0.02)	<0.01 kg/Mg (<0.02)	---	---

[a] Assumes production capacity = 80 percent. Values are in units of kg butadiene emitted per Mg of product or, in the case of equipment leaks, Mg butadiene emitted per year. The numbers in parentheses are in units of pounds butadiene emitted per ton product (lbs/ton) or tons butadiene emitted per year (tons/yr).

[b] Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

[c] Upper value used to prevent disclosing confidential operating capacity.

[d] "---" means no data specific to level or efficiency of controls were available.

presented in Section 4 (Table 8). Emissions are presented in units of megagrams of butadiene emitted per year (Mg/yr) with the English equivalents in tons (tons/yr) appearing in parentheses. Example calculations are provided in Appendix A. The only controls reported in use by the industry are flares and/or rupture discs for pressure relief devices (PRD). Some facilities perform visual inspections but with an unknown frequency. A summary of the available data is given in Table 13.

Secondary Emissions--

Secondary emissions occur at the on-site and off-site facilities that treat and dispose of wastewater, liquid waste, or solid waste. Waste streams may be generated from any of the operations shown in Figure 6. Emissions data are available for 18 of the 21 facilities but are incomplete for each type of waste stream. These data are summarized in Table 13. The emission factor estimates were calculated from information on the flowrate of butadiene (kg/day) in the stream and facility production. Because of its volatility and low solubility, no reduction was included unless butadiene vapors were routed to a control device. Units shown are kilograms of butadiene emitted per megagram of product (kg/Mg) with English unit equivalents (lbs/ton) given in parentheses.

POLYBUTADIENE PRODUCTION

Polybutadiene production consumes approximately 22 percent of the butadiene produced. Like SB elastomer, polybutadiene is primarily used by the tire manufacturing industry, but also finds uses in the high impact resins industry.

Four companies at five locations currently have the capacity to produce polybutadiene, three of which coproduce polybutadiene with styrene-butadiene copolymer.[6] These are listed in Table 14. Firestone in Lake Charles is primarily an SB copolymer producer, therefore emissions are included in the preceding section. Only emissions attributed to the polybutadiene production process are presented in this section.

TABLE 14. POLYBUTADIENE PRODUCTION FACILITIES[6]

Company	Location	Capacity (Mg/yr) in 1988
American Synthetic Rubber	Louisville, KY	70,000[a]
Firestone	Orange, TX	110,000
Firestone	Lake Charles, LA	---[b]
Goodyear	Beaumont, TX	160,000[c]
Polysar	Orange, TX	63,000

[a] Total includes some multipurpose SBR. Capacity due to increase by the end of 1989.

[b] Facility coproduces SB elastomer and polybutadiene rubber, but is primarily dedicated to SB elastomer.

[c] Capacity due to increase an additional 11,340 megagrams in early 1989. Total includes some multipurpose SBR.

Process Description

The polymerization of butadiene can yield several isomeric polymers. The two of commercial significance are the cis-1,4 isomer and, to a much lesser extent, the 1,2 isomer.[7] The majority of polybutadiene is produced by a solution polymerization process, while smaller quantities are produced by an emulsion polymerization process. The relative proportions of the isomers formed are dependent on the catalyst system used and reaction conditions.

The cis-polybutadiene rubber process consists of four basic steps:

1. butadiene and solvent purification,
2. reaction and concentrations,
3. solvent removal, and
4. drying and packaging.

Figure 7 shows a diagram of this process. In Step 1, feed butadiene is dried and combined with a recycled butadiene stream. Solvent, typically hexane or cyclohexane, is also dried along with a recycled solvent stream. In Step 2, these streams are fed to the reactor where polymerization takes place. With solution polymerization, a catalyst such as lithium, sodium, or potassium is used. The overall conversion of the process is greater than 98 percent.[7]

Reactor effluent is fed to the concentrator (Step 3) where any unreacted butadiene is removed for recycle. The product stream leaving the concentrator consists of polybutadiene dissolved in solvent, and is often referred to as "cement." The cement stream leaving the concentrator contains negligible butadiene. In Step 4, the cement is stripped of solvent, which is recycled to solvent purification. Stripping occurs through direct steam contact. The resulting polybutadiene crumb/water stream is dried, compressed, and packaged in Step 5. This process is run both continuously and in batch mode, but the majority of facilities operate continuously.

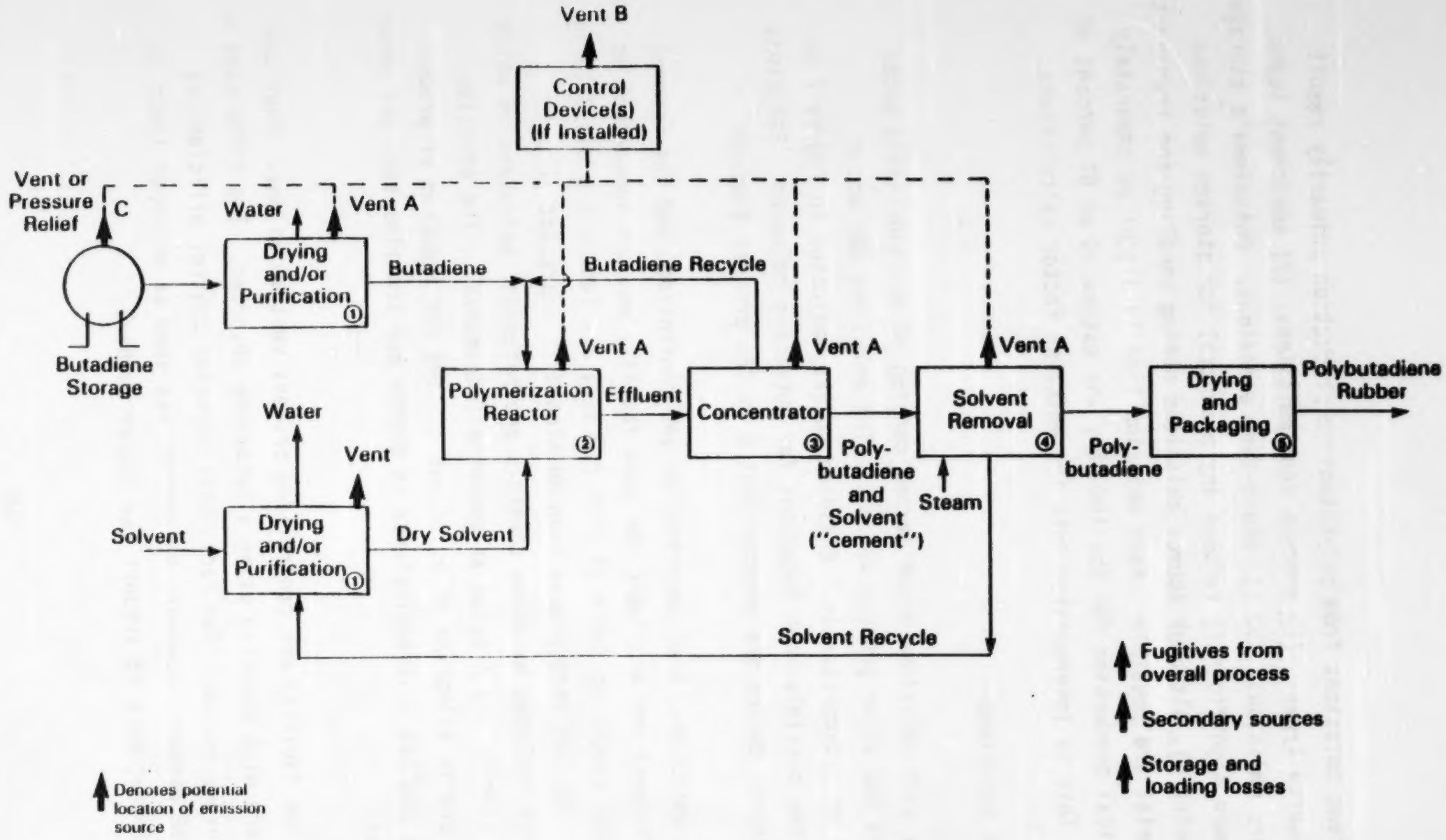
Vent B
Control Device(s) (If Installed)
Vent or Pressure Relief
C
Water
Vent A
Drying and/or Purification ①
Butadiene
Butadiene Recycle
Butadiene Storage
Vent A
Vent A
Vent A
Polymerization Reactor ②
Effluent
Concentrator ③
Solvent Removal ④
Drying and Packaging ⑤
Polybutadiene Rubber
Water
Vent
Poly-butadiene and Solvent ("cement")
Steam
Poly-butadiene
Solvent
Drying and/or Purification ①
Dry Solvent
Solvent Recycle
Fugitives from overall process
Secondary sources
Storage and loading losses
Denotes potential location of emission source

Figure 7. Process Diagram for Production of Polybutadiene Rubber

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Emissions

Butadiene emissions from polybutadiene production primarily result from four source types: (1) process vent emissions, (2) equipment leaks, (3) secondary emissions, and (4) short-term emissions. Butadiene's storage under pressure significantly reduces any potential for storage emissions (emission point C), although source emissions during handling and transport of raw material are possible. Each emission type is discussed separately below. Typical production for the industry was estimated at 81 percent of capacity.[7] This is incorporated into the emission factor calculations.

Process Vent Emissions--

Process vent emissions occur during purging of noncondensible gases from reactors and other process vessels. The emissions may occur continuously or intermittently. Emission points indicated in Figure 7 as Vent A give the possible vent locations for butadiene releases. Emissions after the control device are denoted Vent B in the process diagram.

Data on emissions, both uncontrolled and controlled, and the control type and efficiency are available for each facility and are summarized as emission factor ranges in Table 15 (for raw data see Tables B-9 and B-10 in Appendix B). The two ranges have been developed to represent actual emissions which includes existing controls and potential emissions in which all reported sources are treated as uncontrolled sources. The emission factor units are in kilograms of butadiene emitted per megagram of product (kg/Mg). The English unit equivalents in pounds per ton (lbs/ton) are shown in parentheses.

All but one facility are controlling process vent emissions. Four use at least a flare with one also using a butadiene absorber. The fifth uses a butadiene recovery system. Two facilities reported control efficiencies greater than 98 percent, however, 98 percent was used as an upper limit in the absence of test data to support the higher numbers.

Equipment Leak Emissions--

Equipment leak emissions are estimated by using the number of components, their time in service, and the weight percent butadiene in the stream. Applying the method described in Appendix A to the facility-specific data given in Appendix B, Table B-11, and component-specific emission factors from Table 9, estimated emissions were derived. These results are summarized in Table 15 and represent uncontrolled emissions. Although some facilities perform visual monitoring, none give a specific frequency or scope of these programs; therefore, no estimate of reduction was made. As a result facility emissions equal uncontrolled emissions. The values have units of megagrams butadiene emitted per year (Mg/yr) with the equivalents in English units, tons per year (tons/yr), shown in parentheses.

Secondary Emissions--

Only one facility reported a wastewater stream containing butadiene. Complete evaporation of butadiene from this stream, which is sent to a lagoon, is assumed because of butadiene's volatility and low water solubility. Emissions are estimated at 19.3 Mg/yr, resulting in an emission factor of 0.38 kg butadiene/Mg product. The English equivalent is shown in parentheses. One other facility reports that their wastewater contains no butadiene, therefore produces no emissions. One of the three that indicated they generate solid waste estimated that no butadiene emissions are released. Table B-12 in Appendix B summarizes the facility-specific data.

Short-term Emissions--

Short-term emissions include short-term process vent emissions, pressure relief events, equipment opening losses and accidental releases. Two of the four facilities reported no short-term emissions; each of the other two facilities reported one accidental release. In the first case, the release was a result of a cracked valve; in the second, a loose flange. The estimated losses were 1,360 kg over 30 hours and 5 kg over 5 minutes, respectively.[8]

TABLE 15. SUMMARY OF EMISSION FACTORS FOR POLYBUTADIENE PRODUCTION FACILITIES[7]

Emission Sources	Facility Emission Factors[a,b]		Uncontrolled Emission Factors[a]	
	Range	Mean	Range	Mean
Process Vents	0.00004 - 18.03 kg/Mg (n=6)	3.07 kg/Mg	0.0016 - 18.03 kg/Mg (n=6)	4.48 kg/Mg
	(0.00008 - 36.06)	(6.14)	(0.0032 - 36.06)	(8.96)
Equipment Leaks	3.66 - 28.50 Mg/yr (n=6)	9.44 Mg/yr	3.66 - 28.50 Mg/yr (n=6)	9.44 Mg/yr
	(4.04 - 31.42)	(10.41)	(4.04 - 31.42)	(10.41)
Secondary Sources:				
Wastewater	0 - 0.38 kg/Mg (n=3)	0.12 kg/Mg	0 - 0.38 kg/Mg	0.12 kg/Mg
	(0 - 0.74)	(0.24)	(0 - 0.74)	(0.24)
Solid Waste	0 kg/Mg	---	0 kg/Mg	---

[a] Assumes production capacity = 81 percent. Values are in units of kg butadiene emitted per Mg product or, in the case of equipment leaks, Mg butadiene emitted per year. The numbers in parentheses are in units of pounds butadiene emitted per ton product (lbs/ton) or tons butadiene emitted per year (tons/yr).

[b] Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

ADIPONITRILE PRODUCTION

Adiponitrile (hexanedinitrile) is primarily used as an intermediate in the manufacture of hexamethylenediamine (HMDA) (1,6-diaminohexane), a principal ingredient in nylon 6,6 production.[9] Three facilities currently produce adiponitrile.[10,11] Table 16 identifies their locations and capacities. Only two facilities use butadiene, accounting for 12 percent of butadiene use in the United States.[2] Monsanto which uses acrylonitrile as the starting material is, therefore, not a source of butadiene emissions and is omitted from further discussion.

Process Description

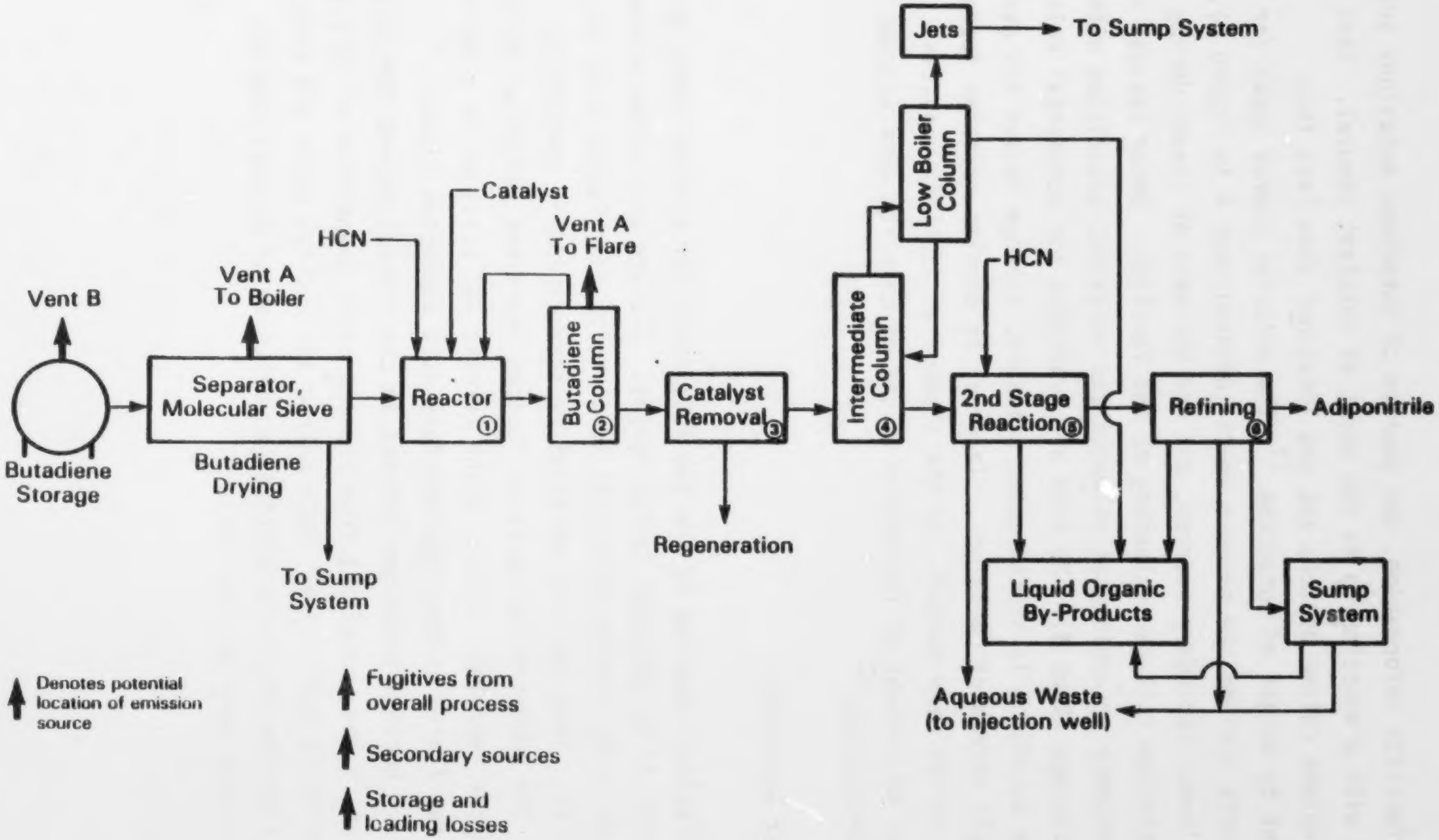
Both facilities run the adiponitrile process on a continuous basis. A generalized process diagram (Figure 8) illustrates the steps in adiponitrile production. Butadiene is first converted to pentenenitriles by the addition of hydrogen cyanide in the presence of a catalyst (Step 1). The resulting pentenenitriles stream then continues through the butadiene column (Step 2) and catalyst removal (Step 3). The intermediary may be sold commercially or refined further. On-site processing begins with distillation of the pentenitriles for use in dinitrile synthesis (Step 4). In the dinitrile system unit (Step 5), the mononitriles are further hydrocyanated for conversion to dinitriles. The resulting mixture of six-carbon dinitriles is refined by distillation (Step 6). The final product, adiponitrile, is stored in tanks and then pumped via pipeline to the HMDA unit for hydrogenation.

Most of the by-products of the process are burned in a boiler to recover their heating value. One of the mononitrile by-products is sold as a commercial product. The butadiene content of this material is reported to be nondetectable with the detection limit falling in the 200-400 ppm range.[10]

TABLE 16. ADIPONITRILE PRODUCTION FACILITIES[4]

Facility	Location	Capacity (Mg/yr) in 1987
DuPont	Orange, TX	484,000
DuPont	Victoria, TX	440,000
Monsanto	Decatur, GA	195,000

[a] Monsanto does not use butadiene as a raw material.


Vent B
Butadiene Storage
Vent A To Boiler
Separator, Molecular Sieve
Butadiene Drying
To Sump System
HCN
Catalyst
Reactor ①
Vent A To Flare
Butadiene Column ②
Catalyst Removal ③
Regeneration
Intermediate Column ④
Low Boiler Column
Jets
To Sump System
HCN
2nd Stage Reaction ⑤
Refining ⑥
Adiponitrile
Liquid Organic By-Products
Sump System
Aqueous Waste (to injection well)
Denotes potential location of emission source
Fugitives from overall process
Secondary sources
Storage and loading losses

Adapted from the process diagram for Du Pont, Victoria, TX

Figure 8. Process Diagram for Production of Adiponitrile

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Emissions

From facility information, the sources of butadiene emissions are associated with production up to the point of catalyst removal. Test data of the butadiene column bottoms (at one location) show less than 0.02 percent by weight of butadiene.[11] The emission source types for which there are data include the process vents (denoted Vent A in Figure 8), equipment leaks, secondary sources, and one estimate of losses during butadiene storage rail car unloading at the facility. Other typical sources include emergency or accidental releases and emissions associated with butadiene storage (Vent B). No data are available for accidental releases and because butadiene is stored under pressure, storage losses are assumed to be a small source of emissions. In order to develop emission factors production values were needed. In the absence of facility-specific information, 80 percent of literature values on capacity were assumed to represent production.[12]

Process Vent Emissions--

The emissions reported by the two facilities for process vents are given in Table 17 as emission factor ranges. All are controlled either by using a flare or by routing emissions to a boiler (see Tables B-13 and B-14 in Appendix B). Thus facility emission factors represent controlled emissions. The uncontrolled emission factors represent potential emissions for the sources reported. Ninety-eight percent was assigned as a maximum efficiency for flares unless supplementary data supported higher efficiencies. Because butadiene content in the process beyond the catalyst removal stage is low, emissions from process vents downstream of this stage are expected to be negligible. Both metric and English units are shown, metric in kilograms butadiene emitted per megagram of product (kg/Mg), English in pounds per ton (lbs/ton).

TABLE 17. SUMMARY OF EMISSION FACTORS FOR ADIPONITRILE PRODUCTION FACILITIES[12]

Emission Sources	Facility Emission Factors[a,b] Range	Facility Emission Factors[a,b] Mean	Uncontrolled Emission Factors[a] Range	Uncontrolled Emission Factors[a] Mean
Process Vents	0.06 kg/Mg (n=2) (0.12)	0.06 kg/Mg (0.12)	2.92 - 3.15 kg/Mg (n=2) (5.84 - 6.30)	3.04 kg/Mg (6.08)
Equipment Leaks	Not available	—	2.47 - 4.76 Mg/yr (n=2) (2.72 - 5.25)	3.62 Mg/yr (3.99)
Secondary Sources	0.008 - 0.012 kg/Mg (n=2) (0.016 - 0.024)	0.01 kg/Mg (0.02)	0.008 - 0.012 kg/Mg (n=2) (0.016 - 0.024)	0.01 kg/Mg (0.02)

[a] Assumes production capacity = 80 percent. Values are in units of kg butadiene emitted per Mg product or, in the case of equipment leaks, Mg butadiene emitted per year. The numbers in parentheses are in units of pounds butadiene emitted per ton product (lbs/ton) or tons butadiene emitted per year (tons/yr). Only incomplete data on emissions were available, therefore, values underestimate emissions.

[b] Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

Equipment Leaks--

Based on facility equipment component counts, their percent time in use, and the percent butadiene in the stream, emissions were estimated following the procedure detailed in Appendix A (individual facility data appear in Table B-15 in Appendix B). Table 17 summarizes uncontrolled emissions for equipment leaks. Controls in use by the two facilities include ambient monitoring, quarterly leak detection and repair (LDAR), double mechanical seals, and pressure relief devices, some of which are routed to a flare. Emissions are in units of megagrams butadiene emitted per year (Mg/yr) with English unit equivalents, tons per year (tons/yr), appearing in parentheses.

Other Emissions--

Although both facilities list various secondary sources, including the use of controls, only two values for emissions are given, one for wastewater, the second for a waste tank (see Table B-16 in Appendix B). Emissions from these sources are reported to be uncontrolled. Other secondary sources reported include butadiene separator blowdown water, waste liquids and a sump tank. Emissions from the latter two are routed to a boiler. Another source identified is the unloading of a storage rail car with a closed vapor balance system, estimated to emit 8.7 Mg/yr.

NEOPRENE PRODUCTION

Neoprene, also called polychloroprene, is a product of chloroprene (2-chloro-1,3-butadiene) polymerization. Consuming approximately 6 percent of butadiene produced,[2] neoprene rubber is primarily used in the automotive industry in such applications as belts, cables, hoses, and wires.[13] Three facilities currently produce neoprene;[14] these are listed in Table 18 along with 1987 capacities. Only two use butadiene as a raw material. Because the DuPont plant in Louisville, Kentucky, starts with chloroprene, it is not included in the subsequent discussion of process and emissions information.[15]

TABLE 18. CHLOROPRENE/NEOPRENE PRODUCTION FACILITIES[14]

Company	Location	Capacity (Mg/yr) in 1987
DuPont[a]	Louisville, KY	90,000[b]
DuPont	La Place, LA	45,000
Denka	Houston, TX	27,000

[a] This facility does not use butadiene as the raw material.

[b] The Kentucky facility has an additional 44,000 tons of idle capacity, but does not use any butadiene.

Process Description

The production of neoprene is a continuous process that starts with the chlorination of butadiene to form chloroprene. Figure 9 shows this process schematically. The initial chlorination (Step 1) takes place in a vapor phase reactor. This produces a mixture of 3,4-dichloro-1-butene (3,4-DCB) and the cis and trans isomers of 1,4-dichloro-2-butene (1,4-DCB), along with unreacted butadiene. The next process step (Step 2) involves the isomerization of 1,4-DCB to 3,4-DCB and the removal of any unreacted butadiene. This is performed in a combined reactor/distillation column under reduced pressure and the presence of a catalyst. Butadiene is recycled to the chlorinator and 1,4-DCB can be recycled or used elsewhere.

The final steps in the synthesis of chloroprene involve the dehydrochlorination of 3,4-DCB in a solution of sodium hydroxide and water (Step 3) and further refining (Step 4). The chloroprene is isolated from the unreacted 3,4-DCB, which is recycled to the reactor. The overall chemical yield of chloroprene is generally greater than 95 percent.[16]

The chloroprene produced is then used in the production of neoprene elastomers. A schematic of this process is shown in Figure 10. Chloroprene proceeds to emulsification (Step 1), then to initiation, catalysis, and monomer conversion in Step 2. The polymer continues with short-stopping and stabilization, monomer recovery and polymer isolation. The resulting latex can be sold as product or is dried and compressed to form neoprene rubber.[15]

Emissions

Of the five general emission types, information is only available for three: process vent releases, equipment leaks, and short-term emissions (including emergency and accidental releases). These sources are discussed in more detail below. Although secondary sources and storage-related emissions have not been characterized, butadiene from pressurized storage tanks is assumed to be negligible and some losses during transfer and

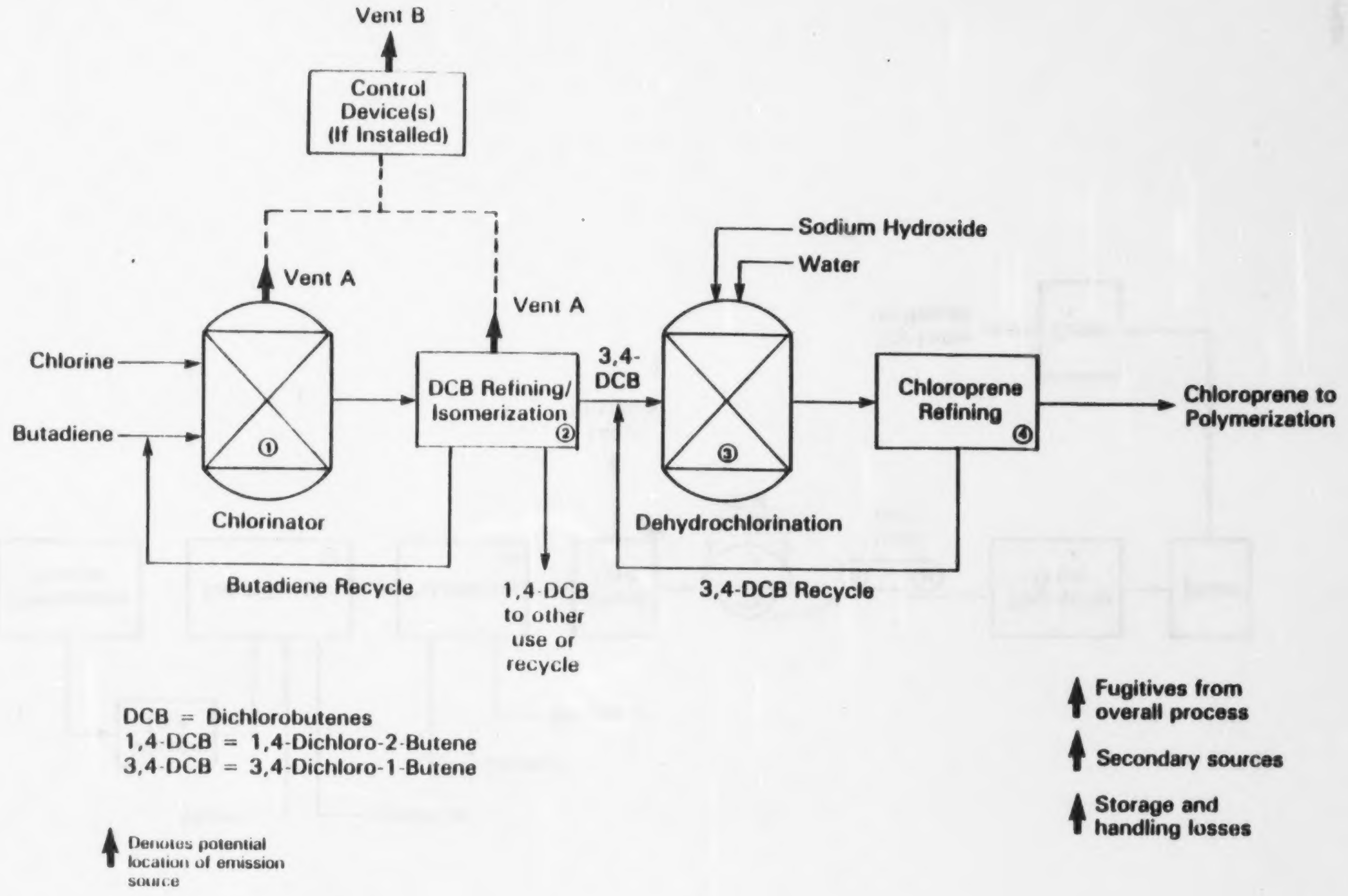
Vent B
Control Device(s) (If Installed)
Vent A
Vent A
Chlorine
Butadiene
①
Chlorinator
Butadiene Recycle
DCB Refining/ Isomerization
②
1,4-DCB to other use or recycle
3,4-DCB
Sodium Hydroxide
Water
③
Dehydrochlorination
3,4-DCB Recycle
Chloroprene Refining
④
Chloroprene to Polymerization
DCB = Dichlorobutenes
1,4-DCB = 1,4-Dichloro-2-Butene
3,4-DCB = 3,4-Dichloro-1-Butene
Denotes potential location of emission source
Fugitives from overall process
Secondary sources
Storage and handling losses

Figure 9. Process Diagram for Production of Chloroprene Monomer

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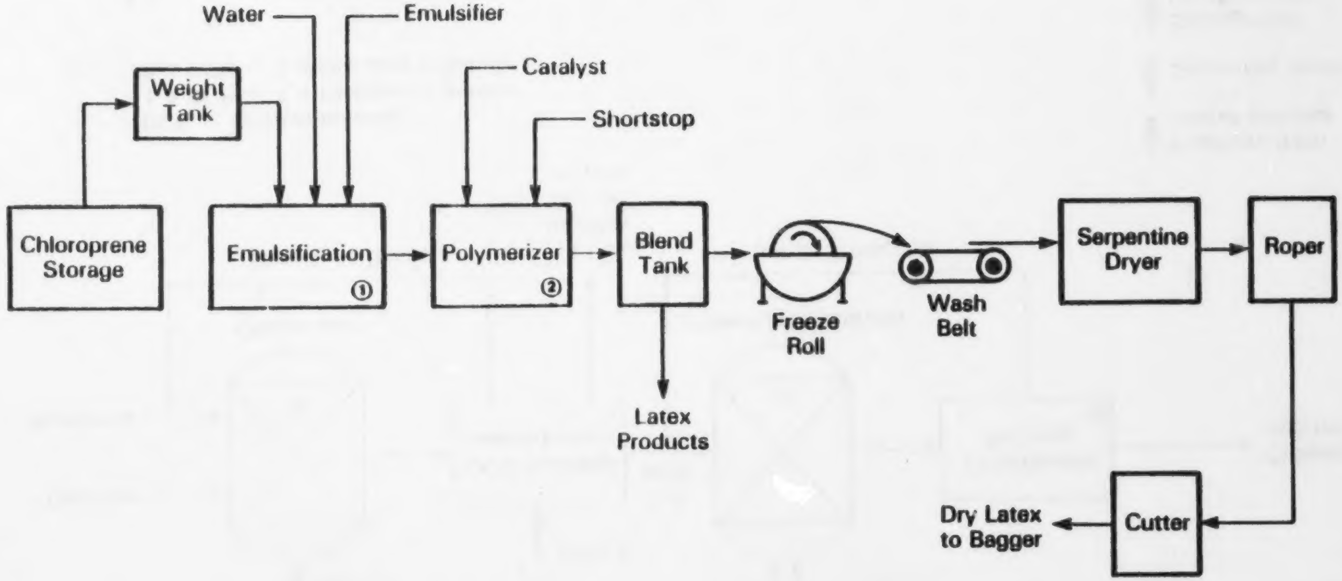
Water
Emulsifier
Catalyst
Shortstop
Weight Tank
Chloroprene Storage
Emulsification
①
Polymerizer
②
Blend Tank
Latex Products
Freeze Roll
Wash Belt
Serpentine Dryer
Roper
Cutter
Dry Latex to Bagger

Figure 10. Flow Sheet for the Production of Neoprene

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handling are likely. For purposes of emission factor development, both facilities were assumed to be operating at full capacity.[15]

Process Vent Emissions--

The two facilities using butadiene report that process vent emissions are limited to the chloroprene production process. These vents are associated with the chlorination, DCB refining and isomerization steps (identified as Vent A in Figure 9) and are used to vent noncondensible gases such as nitrogen. Unreacted butadiene is removed once chlorination is complete and therefore will only be present in low quantities in subsequent process steps. A summary of the data appears in Table 19 as emission factor ranges in kilograms of butadiene emitted per megagram of product (kg/Mg); the equivalent in English units (lbs/ton) are shown in parentheses. The raw data are given in Tables B-17 and B-18 in Appendix B. Calculated as described in Section 4.0, the facility emission factor range reflects use of some controls by both facilities. The uncontrolled emission factor ranges represent potential emissions if the sources reported were not controlled.

Both facilities use controls, but the water-cooled condenser at one affords no emissions reduction. Also, the control efficiency of a flare in use was assigned a 98 percent removal efficiency despite a higher value reported because of the lack of supporting test data. Emissions from control devices are identified as Vent B on the process diagram.

Equipment Leaks--

Using facility-supplied information on the number of equipment components and the procedure in Appendix A, equipment leak emission estimates were calculated (see Table B-18 in Appendix B) and are summarized in Table 19. Emissions are in units of megagrams per year (Mg/yr) with the English unit equivalents given in tons (tons/yr) in parentheses. Although both facilities perform visual and area monitoring, neither provided specific information about these programs. No other controls are reported to be in use.

TABLE 19. SUMMARY OF EMISSION FACTORS FOR NEOPRENE PRODUCTION FACILITIES[15]

Emission Sources	Facility Emission Factors[a,b]		Uncontrolled Emission Factors[a]	
	Range	Mean	Range	Mean
Process Vents	0.16 - 3.89 kg/Mg (n=2) (0.32 - 6.78)	2.02 kg/Mg (4.04)	0.20 - 12.09 kg/Mg (n=2) (0.40 - 24.18)	6.14 kg/Mg (12.28)
Equipment Leaks	0.93 - 4.43 Mg/yr (n=2) (1.03 - 4.88)	2.68 Mg/yr (2.95)	0.93 - 4.43 Mg/yr (n=2) (1.03 - 4.88)	2.68 Mg/yr (2.95)
Secondary Sources	---[c]	---	---	---

[a] Assumes production capacity = 100 percent. Values are in units of kg butadiene emitted per Mg product or, in the case of equipment leaks, Mg butadiene emitted per year. The numbers in parentheses are in units of pounds butadiene emitted per ton product (lbs/ton) or tons butadiene emitted per year (tons/yr).

[b] Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

[c] "---" means no data available.

Short-term Emissions--

As a result of specific requests by the EPA for emissions data, short-term emissions are relatively well characterized. Only emissions that were less than 95 percent controlled were of interest. The data fall into four categories: short-term process vent emissions, pressure relief events, short-term emissions from equipment openings, and emissions from accidental releases.[17] None were routed to a control device. A summary of the estimated emissions is given in Table 20. Additional emissions are possible, because companies were only asked to report the larger releases for that year.

ACRYLONITRILE-BUTADIENE-STYRENE COPOLYMER PRODUCTION

Acrylonitrile-butadiene-styrene (ABS) resins are currently produced by three companies at nine locations.[18] Table 21 presents a list of these facilities with their approximate capacities. The ABS resins are used to make plastic components for a variety of uses, including automotive parts, pipe and fittings, appliances, telephones, and business machines. Butadiene's use in resin production accounts for about six percent of total butadiene consumption.[2]

Process Description

The ABS resins are synthesized by three polymerization processes:[19]

- an emulsion process,
- a suspension process, and
- a continuous mass (bulk) process.

The majority of production is done by batch emulsions. Specialized resins are produced by the suspension process. These two processes are based on an aqueous-phase reaction. In contrast, the continuous mass process, the newest technology, does not proceed in water. This eliminates the need for dewatering and polymer drying and reduces the volume of wastewater treatment required.

TABLE 20. SHORT-TERM EMISSIONS (1984) FROM NEOPRENE PRODUCTION FACILITIES[17]

Facility	Event Description	Number of Events per Year	Duration (minute)	Amount Released per Event (kg)
Denka	Butadiene vent shutdown	1	30	68
	Chlorinator shutdown	4/month	30	11
	Chlorinator shutdown	2/month	30	23
	Pressure relief	0	---	---
	Equipment opening	1	Unknown	<68
	Accidental releases	0	---	---
DuPont	Vent	1	360	132
	Caustic scrubber relief valve	1	Unknown	18
	Equipment opening	0	---	---
	Accidental releases	0	---	---

TABLE 21. ACRYLONITRILE-BUTADIENE-STYRENE RESIN PRODUCTION FACILITIES[18]

Company	Location	Capacity (Mg/yr) in 1988
Borg-Warner	Washington, WV	150,000
Borg-Warner[a]	Ottowa, IL	107,000
Borg-Warner[a]	Port Bienville, MS	91,000
Dow[a]	Midland, MI	77,000
Dow	Hanging Rock, OH	57,000
Dow[a]	Allyn's Point, CT	32,000
Dow[a]	Torrance, CA	32,000
Monsanto	Addyston, OH	191,000
Monsanto	Muscatine, IA	68,000

[a] Facility uses polybutadiene as raw material for ABS production as of 1985.

Emulsion Process--

A block diagram of the ABS emulsion process is shown in Figure 11.[20] This process is referred to as the ABS/SAN (styrene-acrylonitrile) process because SAN is prepared in a side step and mixed with graft ABS. Some companies also produce SAN as a separate product.

The emulsion process involves several steps from combining the raw materials with water for aqueous-phase reaction to purification and packaging of the product resins. Three distinct polymerizations occur in the first few steps:

- butadiene polymerizes to form a polybutadiene substrate latex,
- styrene and acrylonitrile are grafted to the polybutadiene substrate, and
- styrene-acrylonitrile copolymer forms.

About 70 to 90 percent of butadiene monomer is converted to polybutadiene in the first step (Figure 11). The unreacted butadiene monomer is removed from the latex in a flash stripper (Step 2) and usually recovered. The reactor, stripper, and recovery system vents are usually directed to a flare or other combustion device. The grafting of acrylonitrile and styrene to the polybutadiene substrate (Step 3) may be either a batch or continuous process. Reaction conversion of monomers is 90 to 95 percent. Vapors from the reactors are usually vented to an acrylonitrile absorber. The absorber is vented to the atmosphere or an incinerator.

The ABS plastic is a blend of graft ABS rubber and SAN resin. The blend of these compounds determines the desired properties for the ABS product. The copolymer SAN is prepared in a separate side step. The prepared SAN and graft ABS are mixed at either of two points in the process. The SAN latex may be blended with graft rubber latex in the coagulator (Step 4). The agglomerated polymer is dewatered by screening (Step 5), centrifuging (Step 6), and vacuum filtration (Step 7). No drying step is required. However, some facilities employ a dryer in place of the

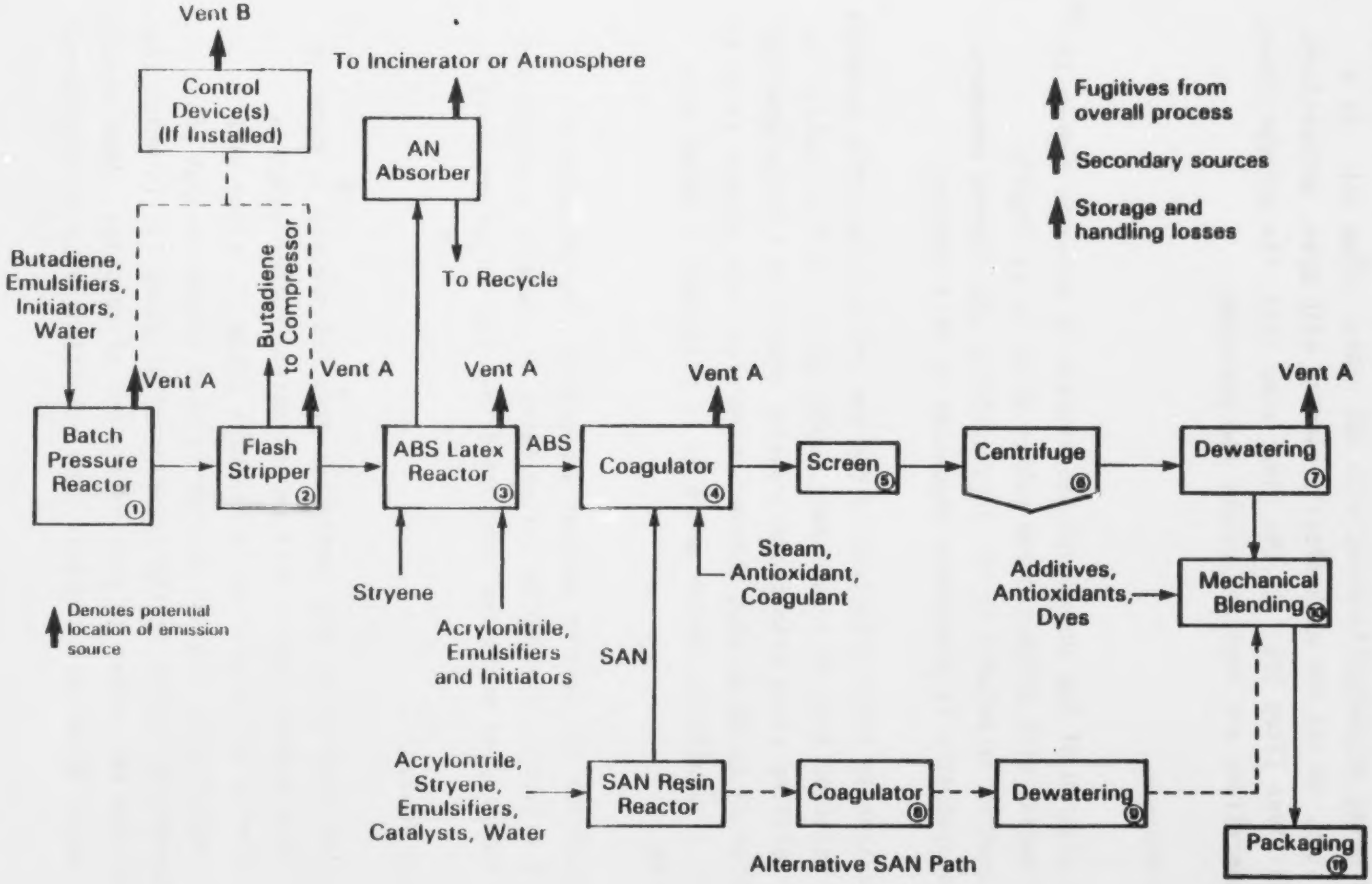
Vent B
Control Device(s) (If Installed)
To Incinerator or Atmosphere
AN Absorber
To Recycle
Fugitives from overall process
Secondary sources
Storage and handling losses
Butadiene, Emulsifiers, Initiators, Water
Butadiene to Compressor
Vent A
Vent A
Vent A
Vent A
Vent A
Batch Pressure Reactor ①
Flash Stripper ②
ABS Latex Reactor ③
ABS
Coagulator ④
Screen ⑤
Centrifuge ⑥
Dewatering ⑦
Steam, Antioxidant, Coagulant
Additives, Antioxidants, Dyes
Mechanical Blending ⑩
Stryene
Acrylonitrile, Emulsifiers and Initiators
SAN
Denotes potential location of emission source
Acrylontrile, Stryene, Emulsifiers, Catalysts, Water
SAN Resin Reactor
Coagulator ⑧
Dewatering ⑨
Packaging ⑪
Alternative SAN Path

Figure 11. Process Diagram for Production of ABS/SAN via the Emulsion Process

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centrifuge and vacuum filter. Alternatively, the SAN latex may be coagulated (Step 8) and dewatered (Step 9) separately with the resulting solid resins being mechanically mixed with ABS rubber (Step 10). In a compounding step, solids are mechanically blended with dyes, antioxidants, and other additives (Step 10). In the final step (11), the polymer sheets from these operations are then pelletized and packaged.

Suspension Process--

A block diagram of the suspension ABS process is shown in Figure 12.[20] This process begins with polybutadiene rubber which is so lightly crosslinked that it is soluble in the acrylonitrile and styrene monomers. Polybutadiene synthesis is previously described in this section.

Polybutadiene is first dissolved in styrene and acrylonitrile monomers to produce a solution free of crosslinked rubber gels. A free-radical is added to the solution along with chain-transfer agents in a prepolymerizer (Step 2). After 25 to 35 percent monomer conversion, the polymer syrup is transferred to a suspension reactor where it is dispersed in water with agitation (Step 3).

After achieving the desired monomer conversion, the products are transferred to a washing/dewatering system (Step 4), usually a continuous centrifuge. The polymer beads are then dried in a hot air dryer (Step 5).

Continuous Mass Process--

A block flow diagram for the continuous mass ABS process is shown in Figure 13.[20] This process begins with polybutadiene rubber which is dissolved in styrene and acrylonitrile monomers (Step 1), along with initiators and modifiers. The ABS polymer is then formed through phase inversion. Conversion begins in the prepolymerizer (Step 2), in which the reaction causes the ABS rubber to precipitate out of solution. When monomer conversion is about 30 percent complete, the resulting syrup is transferred

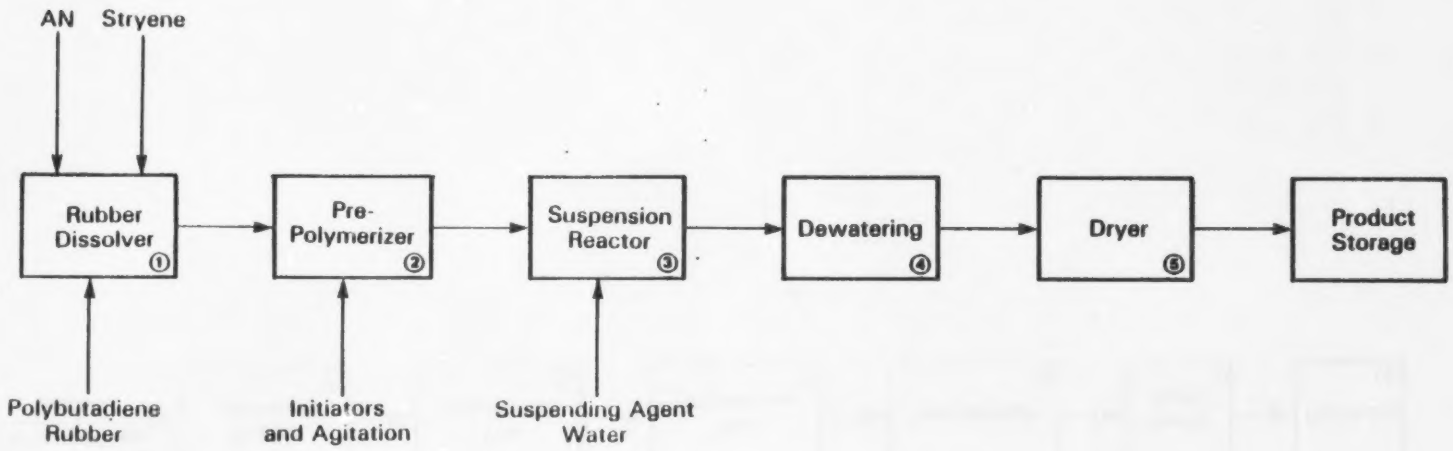
AN
Stryene
Rubber Dissolver ①
Pre-Polymerizer ②
Suspension Reactor ③
Dewatering ④
Dryer ⑤
Product Storage
Polybutadiene Rubber
Initiators and Agitation
Suspending Agent Water

Figure 12. Process Diagram for Production of ABS via the Suspension Process

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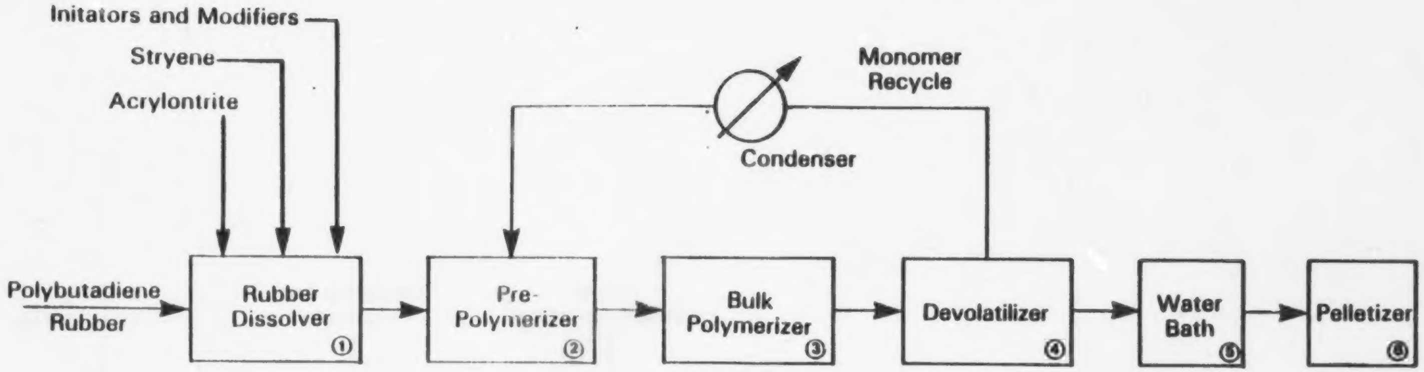
Initators and Modifiers
Stryene
Acrylontrite
Polybutadiene Rubber
Rubber Dissolver ①
Pre-Polymerizer ②
Bulk Polymerizer ③
Devolatilizer ④
Water Bath ⑤
Pelletizer ⑥
Condenser
Monomer Recycle

Figure 13. Process Diagram for Production of Bulk ABS

0981524R

to the bulk polymerizer where monomer conversion is taken to between 50 and 80 percent (Step 3). Unreacted monomer is removed under vacuum from the polymer melt in the devolatilizer (Step 4). The monomer vapors are condensed and recycled to the prepolymerizer. The ABS polymer is then extruded, cooled in a water bath (Step 5), and chopped into pellets (Step 6).

Emissions

At least five of the nine facilities producing ABS do not use butadiene. They start instead from polybutadiene and proceed either through the suspension process or the continuous mass process. Therefore, no butadiene emissions are expected from these production processes. Of the four remaining plants in operation, data are only available for three locations and are limited to information on process vents and equipment leaks associated with the emulsion process. Calculated emission factors (kilograms butadiene emitted per megagram of product, kg/Mg) and annual emission estimates (megagram butadiene emitted per year, Mg/yr) are summarized in Table 22 as ranges and are based on data appearing in Tables B-19 and B-20 in Appendix B. Values in English equivalents are shown in parentheses. Production is assumed to be operating at full capacity.[19] The facility emission factor range for process vents includes existing sources, some of which are controlled. The uncontrolled range represents potential emissions if the sources reported were not controlled.

One estimate of emissions from butadiene storage was reported as zero because butadiene is stored under pressure. Some emissions are possible from secondary sources, emergency and accidental releases, and transfer and handling raw material losses, but estimates for these sources are currently unavailable.

Process Vent Emissions--

Based on available data, process vent emissions of butadiene occur mainly from the flash stripping of the latex from the polymerization reactor

TABLE 22. SUMMARY OF EMISSION FACTORS FOR ABS PRODUCTION FACILITIES[a],[19]

Emission Sources	Facility Emission Factors[a,b]		Uncontrolled Emission Factors[a]	
	Range	Mean	Range	Mean
Process Vents	0.08 - 5.33 kg/Mg (n=3) (0.16 - 10.66)	2.11 kg/Mg (4.22)	3.25 - 5.64 kg/Mg (n=3) (6.50 - 11.28)	4.74 kg/Mg (9.48)
Equipment Leaks	1.10 - 3.17 Mg/yr (n=2) (1.21 - 3.50)	2.14 Mg/yr (2.36)	1.10 - 3.17 Mg/yr (n=2) (1.21 - 3.50)	2.14 Mg/yr (2.36)
Secondary Sources	---[c]	---	---	---

[a] Assumes production capacity = 100 percent. Values are in units of kg butadiene emitted per Mg product or, in the case of equipment leaks, Mg butadiene emitted per year. The numbers in parentheses are in units of pounds butadiene emitted per ton product (lbs/ton) or tons butadiene emitted per year (tons/yr). Data from two facilities are specific to the emulsion process; the third is assumed to use the same.

[b] Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

[c] "-----" means no data available.

in the ABS emulsion process. The vent emissions from the batch reactors are highly variable with changing compositions. Most of these vents are controlled by a flare.

Butadiene emissions also occur during the coagulation and dewatering stages and from intermediate process latex tanks. Only one facility uses a control device and this is limited to one of the downstream vents which is controlled by routing the vent to the plant boiler; others vent to the atmosphere. Figure 11 shows the process vent locations: Vent A for emissions directly associated with the process and Vent B for emissions from a control device.

Equipment Leaks--

The estimates for uncontrolled equipment leaks at the two facilities appearing in Table 22 are based on equipment counts provided by the facilities. The estimation procedure is described in Appendix A. One location reports daily inspection of equipment; however, no further details on follow up for any leaks discovered during these inspections are given.

NITRILE ELASTOMER PRODUCTION

Nitrile elastomer or nitrile-butyl rubber (NBR) is produced by seven facilities, with an eighth due to begin production by the end of 1988.[21] The location of the facilities, the type of elastomer produced, and their approximate capacities are presented in Table 23.

Nitrile elastomer is considered a specialty elastomer and is primarily used for its oil, solvent, and chemical resistant properties by a variety of manufacturers.[22] Some uses include hose, belting, and cable manufacturing, and molded goods such as seals and gaskets. Nitrile elastomer production accounts for about 3 percent of total annual butadiene consumption.[2]

Several of the facilities involved in NBR production also produce other elastomers. Goodyear in Texas, Polysar in Tennessee, Copolymer, and

TABLE 23. NITRILE ELASTOMER PRODUCTION FACILITIES[21]

Company	Location	Elastomer Type	Capacity (Mg/yr dry rubber or latex) in 1988
Copolymer	Baton Rouge, LA	Unknown	6,000
B. F. Goodrich	Louisville, KY	Solid rubber	32,500
Goodyear	Houston, TX	Solid rubber	23,000
Goodyear	Akron, OH	Solid rubber, latex	6,000
Polysar, Ltd.	Orange, TX	Solid rubber	1,600[a]
Polysar Latex Division	Chattanooga, TN	Latex	5,000
Reichhold Chemicals	Cheswold, DE	Latex	5,000
Uniroyal Chemical Co.	Painesville, OH	Solid rubber	20,000

[a] Due on line by the end of 1988.

Reichhold all produce styrene-butadiene copolymers. The Polysar facility in Orange, Texas, due to begin nitrile elastomer production in 1988, already produces polybutadiene. Because of the common use of butadiene in these production processes, emissions data often represent total rather than individual process emissions. Whenever possible, the portion of butadiene emissions directly attributable to nitrile rubber is shown.

Process Description

Nitrile elastomers are copolymers of acrylonitrile and butadiene. They are produced by emulsion polymerization in batch or continuous processes. The process is illustrated in the block flow diagram, Figure 14.[20]

The emulsion polymerization process uses water as a carrier medium. Butadiene and acrylonitrile monomers are piped to agitated polymerization reactors (Step 1) along with additives and soap. The water not only serves as a reaction medium, but also effectively transfers the heat of reaction to the cooled reactor surfaces. The additives include a catalyst (cumene hydroperoxide as an oxidizing component), sodium formaldehyde sulfoxylate with EDTA (ferrous sulfate complexed with ethylenediamine-tetraacetic acid) as the reducing component, and modifiers (alkyl mercaptans).

The reaction is allowed to proceed for 5 to 12 hours. A shortstop solution (sodium bisulfate or potassium dimethyl dithiocarbonate) is added to terminate the reaction at a predetermined point, usually after 75 to 90 percent conversion (depending upon the desired molecular weight of the product). The reaction latex is then sent to a blowdown tank (Step 2) where antioxidants are normally added.

The latex is subjected to several vacuum flash steps (3) where most of the unreacted butadiene is released. It is then steam stripped under vacuum (Step 4) to remove the remaining butadiene and most of the unreacted acrylonitrile. The unreacted monomers are sent to recovery and recycle. Stripped latex at about 110 to 130°F is pumped to blend tanks (Step 5).

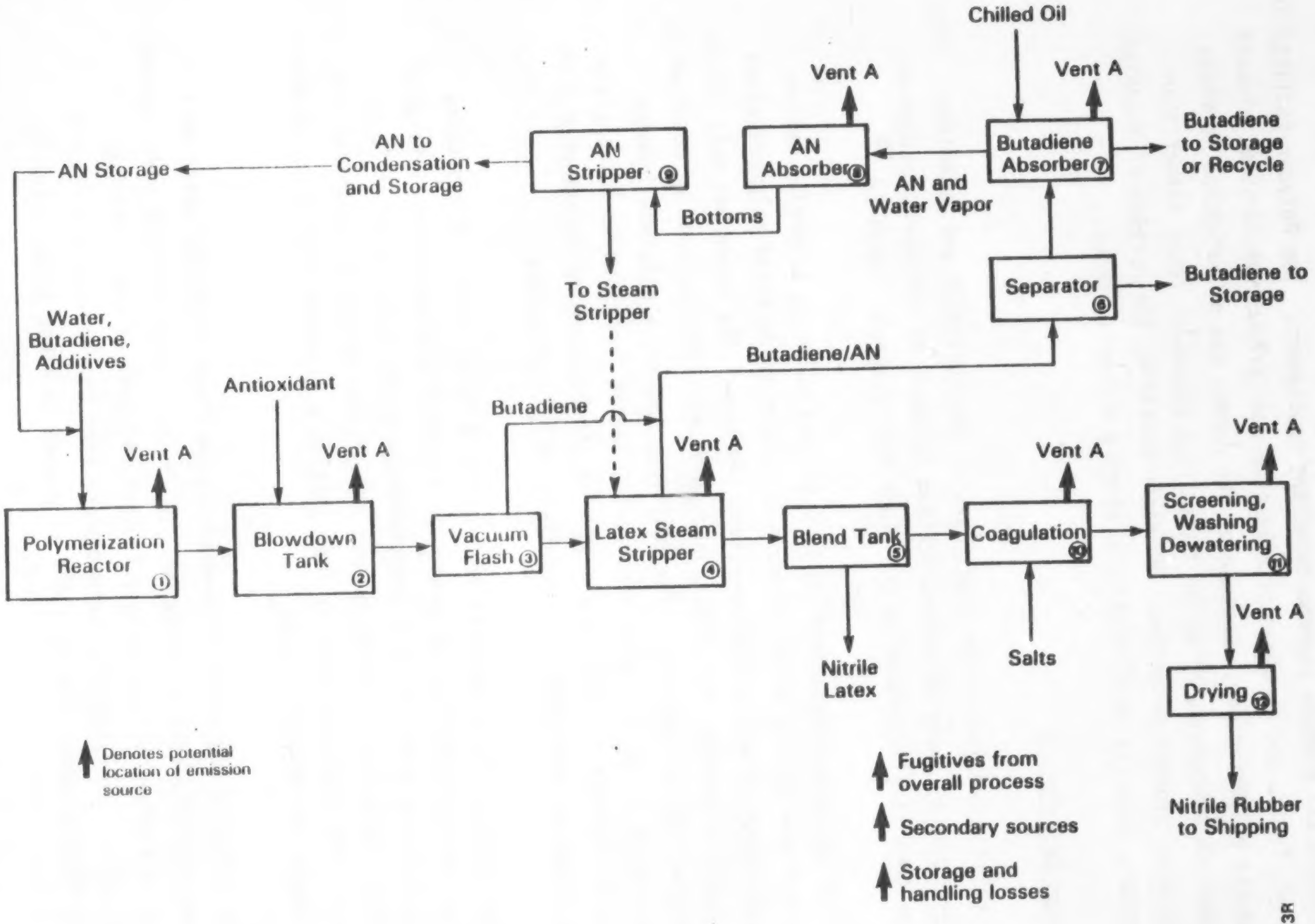
Chilled Oil
Vent A
Vent A
AN Storage
AN to Condensation and Storage
AN Stripper ⑨
AN Absorber ⑧
Butadiene Absorber ⑦
Butadiene to Storage or Recycle
AN and Water Vapor
Bottoms
To Steam Stripper
Separator ⑥
Butadiene to Storage
Water, Butadiene, Additives
Butadiene/AN
Antioxidant
Butadiene
Vent A
Vent A
Vent A
Vent A
Vent A
Polymerization Reactor ①
Blowdown Tank ②
Vacuum Flash ③
Latex Steam Stripper ④
Blend Tank ⑤
Coagulation ⑩
Screening, Washing Dewatering ⑪
Vent A
Nitrile Latex
Salts
Drying ⑫
Denotes potential location of emission source
Fugitives from overall process
Secondary sources
Storage and handling losses
Nitrile Rubber to Shipping
0981523R

Figure 14. Process Diagram for Production of Nitrile Elastomer

Gases released in the flash steps and stripped overhead contain butadiene. These are sent to a partial condenser (not shown) and separator (Step 6) where butadiene vapor is condensed and sent to liquid storage. Uncondensed butadiene vapor from the separator flows to an absorber (Step 7) where it is absorbed by countercurrent contact with chilled oil. The absorber bottoms are pumped to a flash tank (not shown) and dissolved butadiene is released and returned to the compressor. The hot lean oil is then cooled, chilled, and returned to the top of the absorber.

Unreacted acrylonitrile in flash vapors and latex stripper overhead is recovered by sending these gases to a water absorber (Step 8). Absorber bottoms and the liquid phase of the latex stripper overhead are pumped to a steam stripper (Step 9). The overhead vapor stream from this stripper is condensed in a decanter. Phase separation is allowed to take place and the acrylonitrile phase is decanted to storage while the water-rich phase with residual acrylonitrile is returned to the stripper.

Latex is pumped from the blend tanks (Step 5) to a coagulation tank (Step 10) where the emulsion is broken by the addition of dilute inorganic salt solution (sodium chloride or aluminum sulfate) or a weak organic acid. The slurry of fine polymer crumb is then filtered to remove coagulating chemicals (liquor is recycled) and may be reslurried for further purification. Crumb is dewatered in an extruder (Step 11), then hot air dried (Step 12). Dried rubber is weighed, pressed into bales, and prepared for shipment.

If latex is the desired end product, the final processing steps (coagulation, screening, washing, and drying) are omitted. The initial steps are essentially identical to those for solid rubber production.[19]

Emissions

The availability of emissions data is somewhat limited. At coproduction facilities, the estimated butadiene emissions include releases from other elastomer production processes. For the two facilities which are also SB copolymer producers, the percent of the total reported emissions assigned to the NBR process is based on the percent of total production resulting in nitrile elastomer in 1984. Table 24 summarizes emissions information for process vents, equipment leaks, and secondary sources. All nitrile elastomer production is assumed to be operating at full capacity.[19] Emissions from emergency and accidental releases and transfer/handling are not known and storage vent emissions from butadiene storage are expected to be low because of the use of tanks under pressure.

Process Vent Emissions--

All six facilities for which emissions data were reported use some level of emissions control. Many of the controls which are designed to reduce acrylonitrile emissions are also effective in reducing butadiene emissions (for example, flares). Data from four of these are summarized as emission factor ranges in Table 24 (see Tables B-21 and B-22 in Appendix B for facility-specific data). The fifth is not used because calculation of an emission factor might reveal company confidential information on production capacity. Potential vent locations shown in Figure 14 as Vent A are based on information on the vent locations supplied by five facilities.

The emission factor ranges have been developed as described in Section 4.0. The facility emission factor range includes the various levels of control that each facility has in place. The uncontrolled emission factor range represents potential emissions if controls were not in use. The units shown are in kilograms butadiene emitted per megagram of product (kg/Mg) and the English unit equivalents (lbs/ton) appear in parentheses.

Equipment Leaks--

The estimates for equipment leaks provided by three facilities span three orders of magnitude (Table 24). The only known control devices currently in use are rupture discs and a flare for pressure relief devices by one facility. The other three facilities indicate daily visual inspection of equipment; however, no repair programs are described for any

TABLE 24. SUMMARY OF EMISSION FACTORS FOR NITRILE ELASTOMER PRODUCTION FACILITIES[19]

Emission Sources	Facility Emission Factors[a,b]		Uncontrolled Emission Factors[a]	
	Range	Mean	Range	Mean
Process Vents	0.0001 - 8.90 kg/Mg (n=6) (0.0004 - 17.80)	~ 2 kg/Mg[c] (~ 4)	0.01 - <25 kg/Mg (n=6) (0.030 - <50)	~ 8 kg/Mg[c] (~ 16)
Equipment Leaks	Not available	—	0.39 - 16.93 Mg/yr (n=3) (0.43 - 18.67)	7.93 Mg/yr (8.74)
Secondary Sources[d]	0.001 - 0.009 kg/Mg (n=2) (0.002 - 0.018)	0.005 kg/Mg (0.010)	0.001 - 0.009 kg/Mg (n=2) (0.002 - 0.018)	0.005 kg/Mg (0.010)

[a] Assumes production capacity = 100 percent. Values are in units of kg butadiene emitted per Mg product or, in the case of equipment leaks, Mg butadiene emitted per year. The numbers in parentheses are in units of pounds butadiene emitted per ton product (lbs/ton) or tons butadiene emitted per year (tons/yr). Only incomplete data on emissions were available, therefore, values underestimate emissions.

[b] Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

[c] Upper value used to prevent disclosing confidential operating capacity.

[d] Lower end of range is for one solid waste stream; upper end includes solid waste, wastewater and contaminated cooling water.

of the leaks found. Although some controls are in place, detailed information to apply during emissions estimation was not available. Therefore, only calculations for potential emissions have been done. These are in units of megagram butadiene emitted per year (Mg/yr) with English unit equivalents (tons/yr) given in parentheses.

Secondary Emissions--

One emissions estimate from secondary sources of 60 kg/yr was provided.[19] This estimate includes the following sources: wastewater, solid waste, and contaminated cooling water. A second facility also indicated wastewater and solid waste as potential secondary sources.[19] The butadiene content in the wastewater is undetermined, therefore, emissions cannot be estimated. However, the solid waste stream contains 4 ppm butadiene. Based on a generation rate of 1063 lbs/day and assumptions of continuous operation and total volatilization, the source's emission potential is approximately 20 kg/yr.[23]

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SECTION 6

BUTADIENE EMISSIONS FROM MOBILE SOURCES

This section summarizes recent work by the Office of Mobile Sources which has quantified butadiene as one component of vehicle hydrocarbon emissions. Butadiene emissions are formed in vehicle exhaust by the incomplete combustion of the fuel. As a rule, refiners try to minimize the level of butadiene in gasoline and diesel fuel because it tends to readily form a varnish which can be harmful to engines. Therefore, the majority of gasoline and diesel fuel should have no significant butadiene content. As a result, it is assumed that butadiene is not present in vehicle evaporative or refueling emissions.

Recent work by the U. S. EPA Office of Mobile Sources (OMS) on the percent butadiene in vehicle exhaust hydrocarbon emissions refines previous estimates made by this office.[1] The new percent, 0.35 percent, is based on data from light-duty, three-way catalyst-equipped vehicles. In the absence of reliable test data for other vehicle classes, OMS applied this percent to MOBILE3-predicted exhaust hydrocarbon emission factors for all vehicle classes to obtain butadiene emission factors. These are given in Table 25.

Based on the limited data available, butadiene emissions appear to increase roughly in proportion to hydrocarbon emissions. Since hydrocarbon emissions from noncatalyst-equipped vehicles are greater than their catalyst-equipped counterparts, butadiene emissions are expected to be higher from noncatalyst-equipped vehicles.

TABLE 25. VEHICLE EMISSION FACTORS FOR 1,3-BUTADIENE EMISSIONS[1]

	Emission Factors (g butadiene/mile driven)		
Vehicle Class	1980	1995 No I/M[a]	1995 With I/M
Light-duty Gas Vehicle	0.0127	0.0041	0.0028
Light-duty Gas Truck	0.0205	0.0087	0.0055
Heavy-duty Gas Vehicle	0.0328	0.0089	0.0089
Heavy-duty Diesel Vehicle	0.0159	0.0086	0.0086

[a] I/M means inspection and maintenance program.

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SECTION 7
EMISSIONS FROM MISCELLANEOUS SOURCES OF BUTADIENE

This section provides an overview of the miscellaneous sources of butadiene emissions. These sources may be divided into three categories: butadiene use in manufacturing, indirect sources, and "other." With regard to the first category, Section 5 already discusses the major uses of butadiene; this section identifies the smaller consumers that account for about two percent of butadiene use in the United States. Available details of the production process and associated emissions will be provided, where known. Often these details are incomplete; therefore, readers should contact the facilities directly for the most accurate information.

Information on indirect sources (that is, processes that produce butadiene as a by-product or where butadiene appears as an impurity) is limited and any associated emission estimates are even more scarce. A few stationary sources, however, have been identified and are described briefly in the second half of this section.

The third category, "other," encompasses situations where butadiene may be present as an impurity which may, therefore, be potential butadiene sources. However, these could not be classified otherwise for lack of readily available information.

MISCELLANEOUS USES OF BUTADIENE IN CHEMICAL PRODUCTION

Eighteen companies at 20 locations are producing 14 different products from butadiene. Originally identified in a summary report on miscellaneous butadiene uses,[1] this list has been updated using the 1987 Directory of Chemical Producers - U.S.A.[2] These facilities are summarized in Table 26, along with estimated capacities. Because data corresponding to each location are not readily available, all the production process descriptions,

TABLE 26. MISCELLANEOUS USES OF BUTADIENE IN CHEMICAL PRODUCTION[1,2,3]

Company	Location	Product	Mode of Operation	1986 Design Capacity (Mg/yr)
Ameripol Synpol	Port Neches, TX	Styrene-butadiene-vinylpyridine (SBV) Latex	Unknown	—[a]
ArChem Company	Houston, TX	Tetrahydrophthalic (THP) Anhydride	Batch	515
B. F. Goodrich Company	Akron, OH	Butadiene-vinylpyridine Latex	Batch (on demand)	—
Borg-Warner Chemicals Company	Washington, WV	Methyl Methacrylate-butadiene-styrene (MBS) Resins[b]	Unknown	—
Calhio Chemicals	Perry, OH	Captan^{R}	Batch	—
Chevron Chemical	Richmond, CA	Captafol^{R}	Continuous	—
DuPont	Beaumont, TX	1,4-Hexadiene	Continuous	---[c]
DuPont	Victoria, TX	Dodecanedioic Acid	Continuous (2 weeks per month due to low demand)	---
		Butadiene Dimers	Unknown	—
GenCorp	Mogadore, OH	SBV Latex	Unknown	—
Goodyear	Akron, OH	SBV Latex	Unknown	—
Goodyear	Calhoun, GA	SBV Latex	Unknown	—
Kaneka Texas Corporation	Bayport, TX	MBS Resins	Batch	24,000[d]
Metco America	Axis, AL	MBS Resins	Unknown	—
Mobay Synthetics Corporation[e]	Houston, TX	THP Acid	Batch	1,500

TABLE 26. (Continued)

Company	Location	Product	Mode of Operation	1986 Design Capacity (Mg/yr)
Phillips Chemical Company	Borger, TX	Butadiene Cylinders[b]	Batch	485
		Butadiene-furfural Cotrimer[b]	Continuous, intermittent, about 65% of the time	45
		Sulfolane	Batch	—
Pony Industries	West Chester, PA	Butadiene Dimers	Unknown	—
Rohm and Haas Company	Louisville, KY	MBS Resins	Batch	---
Shell Oil Company	Norco, LA	Sulfolane	Unknown	—
Standard Oil Chemical Company	Lima, OH	Methyl Methacrylate-acrylonitrile-butadiene-styrene (MABS) Polymer	Unknown	—
Union Carbide	Institute, WV	Butadiene Dimers	Continuous	6,500
		Ethylidene Norbornene	Continuous	—

[a] "___" capacity not known.

[b] In operation in 1984, status unknown in 1987.

[c] "---" means company confidential.

[d] Increased capacity due on-line by the end of 1987.

[e] Formerly Denka.

current as of 1984, appear first, followed by a summary of any emissions estimates.

Product and Process Descriptions

Styrene-Butadiene-Vinylpyridine (SBV) Latex--

No information on the production process or use of styrene-butadiene-vinylpyridine latex is available. As a copolymer, the production is likely to be similar to that of other copolymers.

Tetrahydrophthalic (THP) Anhydride and Acid--

Tetrahydrophthalic anhydride and acid (the acid is the hydrate form of the chemical) may be used either as a curing agent for epoxy resins or as an intermediate in the manufacture of Captan®, an agricultural fungicide.

In the manufacture of the anhydride as a curing agent, Mobay Synthetics (formerly Denka) is reported to use the following process. Liquid butadiene is first pressure fed to a vaporizer. The resulting vapor is then pressure fed to the reactor where reaction with molten maleic anhydride occurs. Maleic anhydride is consumed over a period of 6 to 10 hours. The product, molten THP anhydride, is crystallized onto a chill roller at the bagging operation. Solidified anhydride is cut from the roller by a doctor blade into a weighed container, either a bag or drum.[4] Because ArChem also uses THP anhydride in epoxy resins, use of a process similar to Mobay Synthetics' is assumed.[1]

Calhio was reported to generate the anhydride for captive use as an intermediate for Captan®. In the generation process, butadiene is charged to reactors along with maleic anhydride to produce THP anhydride. The reaction is a Diels-Alder reaction run under moderate temperature and pressure.[5]

Butadiene-Vinylpyridine Latex--

Butadiene-vinylpyridine latex is produced at the B. F. Goodrich, Akron, Ohio facility as an ingredient in an adhesive promoter. As a copolymer, the production process is similar to that of other copolymers, usually involving an emulsion polymerization process.[6] B. F. Goodrich operates the process in a batch mode, on a schedule that depends on demand.

The finished latex is blended with SB latex and a phenol-formaldehyde mixture to form a "dip" or an adhesive promoter. Dip is used with fabrics in geared rubber goods manufacturing. This includes fabric use in tires, hoses, and belting production.[6]

Methyl Methacrylate-Butadiene-Styrene (MBS) Terpolymers--

Methyl methacrylate-butadiene-styrene terpolymers are produced in resin form by four companies at four locations. This resin is used as an impact modifier in rigid polyvinyl chloride products for applications in packaging, building, and construction.[1]

Production of MBS terpolymers is achieved using an emulsion process in which methyl methacrylate and styrene are grafted onto a styrene-butadiene rubber. The product is a two-phase polymer.[7]

Captan®--

In Captan® production, tetrahydrophthalic anhydride is passed through an ammonia scrubber to produce tetrahydrophthalimide (THPI). Molten THPI is coated onto a chill roller where it solidifies into a quasi-crystalline state.

Tetrahydrophtalimide is then conveyed into a reactor containing perchloromethyl mercaptan (PMM). Caustic is charged to the reactor initiating the reaction that produces Captan®. Captan® is brought to a higher temperature in the heat treatment tank to remove residual PMM, after which the material passes through a vacuum filter to remove salt and water. The product cake is dried and collected in a baghouse.[5]

Captafol®--

Chevron produces Captafol®, a fungicide, under the trade name Difolatan® at their Richmond, California facility. The only information on the process is that production occurs on a continuous basis and is carried out in a pressurized system vented to an incinerator.[1]

1,4-Hexadiene--

DuPont produces 1,4-hexadiene for use in manufacturing Nordel® synthetic rubber. Nordel® polymer is used in the manufacture of rubber goods, wire and cable insulation, automotive bumpers, and as an oil additive.[8]

In the reactor, butadiene reacts with ethylene to form 1,4-hexadiene. After reaction, unreacted 1,3-butadiene and ethylene, along with 1,4-hexadiene and by-products, are flashed from the catalyst and solvent. The maximum temperature in the process is approximately 250°F. The catalyst solution is pumped back to the reactor; vaporized components are sent to a stripper column. The column separates ethylene and 1,3-butadiene from the 1,4-hexadiene product and by-products; unreacted components are pumped back to the reactor. The 1,4-hexadiene and by-products are sent to crude product storage before transfer to refining. The 1,4-hexadiene is refined in low-boiler and high-boiler removal columns and transferred to the "Nordel®" polymerization process.[8]

Dodecanedioic Acid (DDDA)--

Dodecanedioic acid is produced by DuPont to use as an intermediate in the production of 1,5,9-cyclodecatriene, a constituent in the manufacture of DuPont's Quiana® fabric.[9] Butadiene can be converted into several different cyclic or open chain dimers and trimers depending upon the reaction conditions and catalysts. Although vinylcyclohexene and 1,5-cyclooctadiene are the predominant products, 1,2-divinylcyclobutane may be formed under suitable reaction conditions. Nickel catalysts are often used in the cyclodimerization and cyclotrimerization of butadiene; however, complexes of iron, copper (I), zeolite, and compositions also promote cyclodimerization, often giving cyclooctadiene as the principal product.[9]

Butadiene Cylinders--

Phillips Chemical Company fills cylinders with butadiene monomer at their Borger, Texas, facility. The NIOSH survey report on this facility indicates that these cylinders may be samples of butadiene taken for process quality control.[10] The report describes routine quality control sampling in the tank farm area in which the samples are collected using pressure cylinders. Operators connect the sample containers to a process line and open valves to fill the cylinder. Butadiene fills the container and is purged out of the rear of the cylinder before the valve is closed, resulting in emissions from the cylinder. The sample container is subjected to vacuum exhaust under a laboratory hood at the conclusion of sampling.[1]

Butadiene Furfural Cotrimer--

Butadiene furfural cotrimer or 2,3,4,5-bis(butadiene)tetrahydrofurfural, commonly known as R-11, is used as an insect repellant and as a delousing agent for cows in the dairy industry. The concentrations of R-11 in commercial insecticide spray is generally less than one percent.[10]

Production of R-11 at the Phillips' Borger, Texas, facility, occurs intermittently throughout the year; however, when operating, the production process is a continuous operation. In the process, butadiene reacts with an excess of furfural in a liquid-phase reactor. The reaction proceeds under moderate conditions of temperature and pressure and consumes 1 mole of furfural for 2 moles of butadiene. After a period of 4 to 5 hours, the reaction mixture is transferred to the reactor effluent surge tank. The mixture proceeds to a vertical column that separates butadiene dimer by distillation. Butadiene dimer, or 4-vinyl-1-cyclohexane, is recovered from the column and later transported to a refinery for reprocessing in crude catalytic cracking units.[10]

Furfural is removed from the reaction products by distillation in a similar column and recycled to the reactor. The last column in the R-11 process runs as a batch operation, and separates R-11 from the polymer kettle product. The kettle product is a crystalline solid which is disposed of in an on-site landfill. R-11, which is in the form of a yellow liquid, is transferred to storage tanks and shipped to customers in drums.[10]

Sulfolane--

Sulfolane is a trade name for tetrahydrothiophene-1,1-dioxide. It is used principally as a solvent for extracting aromatic hydrocarbons from mixtures containing straight-chained hydrocarbons. Sulfolane is produced by first reacting butadiene and sulfur dioxide to form 3-sulfolene. The 3-sulfolene is then hydrogenated to produce Sulfolane. Phillips Chemicals' Borger, Texas, facility is assumed to be using a similar process since it is listed in Reference 2 as also producing Sulfolene. The Shell facility at Norco, Louisiana, has a Sulfolane production unit downstream of the butadiene recovery process that is included as part of the butadiene production facility.[11]

Methyl Methacrylate-Acrylonitrile-Butadiene-Styrene (MABS) Polymers--

Methyl methacrylate-acrylonitrile-butadiene-styrene polymers are produced by Standard Oil Company under the trade name Barex®. The MABS copolymers are prepared by dissolving or dispersing polybutadiene rubber in a mixture of methyl methacrylate-acrylonitrile-styrene and butadiene monomer. The graft copolymerization is carried out by a bulk or a suspension process. The final polymer is two phase, with the continuous phase terpolymer of methyl methacrylate, acrylonitrile, and styrene grafted onto the dispersed polybutadiene phase.[7]

These polymers are used in the plastics industry in applications requiring a tough, transparent, highly impact-resistant, and thermally formable material. Except for their transparency, the MABS polymers are similar to the opaque acrylonitrile-butadiene-styrene plastics. The primary function of methyl methacrylate is to match the refractive indices of the two phases, thereby imparting transparency.[7]

Butadiene Dimers--

Tetrahydrobenzaldehyde (THBA), a butadiene dimer, is produced by Union Carbide, DuPont (Victoria, Texas) and Pony Industries. At Union Carbide, butadiene is reacted with acrolein and cyclohexane to produce THB anhydride in 90+ percent yields over a short period of time when the reaction is carried out at temperatures up to 200°C.[12] The reaction will also take place at room temperature in the presence of an aluminum-titanium catalyst. A by-product of the reaction is 4-vinyl-1-cyclohexane.[12] At Union Carbide's facility, THBA is recovered and the unreacted raw materials are recycled to the feed pot. The feed pot, reactor, recovery stills, and refined product storage tanks are all vented to a flare header.[1] In the absence of process information at the DuPont and Pony Industries facilities, they are assumed to be using a similar production process.

Ethylidene Norbornene (ENB)--

Ethylidene norbornene, produced by Union Carbide, is a diene used as a third monomer in the production of ethylene-propylene-dimethacrylates. Ethylene-propylene-dimethacrylate elastomers are unique in that they are always unsaturated in the side chain pendant to the main or backbone chain. Therefore, any oxidation or chemical reaction with residual unsaturation has only a limited effect on the properties of the elastomer.[13]

Emissions

No emissions data are available for the following products: SBV latex, Captan®, Captafol®, THP Acid, and Ethylidene Norbornene. For processes where emissions information is available, it is limited to three sources: process vents, equipment leaks, and secondary sources.[1,11] Butadiene emissions from raw material storage are expected to be negligible since butadiene is usually stored under pressure. Some emissions resulting from accidental and emergency releases and transfer and handling of raw materials are likely; however, they have not generally been quantified.

Data are available for process vent emissions from eight production processes. At five of these facilities, flares or boilers are used on some vents to control emissions. At a sixth facility, emissions reduction is achieved by recovery of the vented stream off the butadiene-furfural cotrimer process, one of the two process vents identified. Because every facility did not report an emissions estimate for each process vent listed, emissions data are incomplete.

The emission factors for process vents and secondary sources are summarized as ranges in Table 27, with facility-specific data appearing in Tables B-23 through B-25 in Appendix B. The facility emission factor range includes the various levels of control that each facililty has in place. The uncontrolled emission factor range represents potential emissions if controls were not in use. The units shown are in kilograms butadiene emitted per megagram of product (kg/Mg) with the English unit equivalents (lbs/ton) appearing in parentheses.

Because equipment count data were not readily available, no calculations of equipment leak emissions using average CMA factors was done. Instead, emissions as reported in the summary memoranda are shown here.[1,11] Equipment leaks were estimated for eight processes at eight facilities. Using equipment counts grouped according to the percent butadiene in the streams, the time in service for each component, and EPA emission factors

TABLE 27. SUMMARY OF EMISSION FACTORS FOR MISCELLANEOUS CHEMICALS PRODUCTION FACILITIES[1,6,11]

Chemical Produced	Source	Facility Emission Factors[a,b]		Uncontrolled Emission Factors[a]	
Butadiene cylinders	Process Vents	21.6 kg/Mg	(43.2)	21.6 kg/Mg	(43.2)
	Equipment Leaks	<0.1 Mg/yr	(<0.11)	<0.1 Mg/yr	(<0.11)
	Secondary Sources	Not reported		——	
Butadiene dimers	Process Vents	0.015 kg/Mg	(0.030)	0.77 kg/Mg	(1.54)
	Equipment Leaks	3.9 Mg/yr	(4.3)	Not available	
	Secondary Sources	0		0	
Butadiene-furfural cotrimers	Process Vents	220 kg/Mg	(440)	220 kg/Mg	(440)
	Equipment Leaks	0.5 Mg/yr	(1.1)	Not available	
	Secondary Sources	0		0	
Butadiene-vinylpyridine latex	Process Vents	-----[c]		-----[c]	
	Equipment Leaks	0.55 Mg/yr	(0.61)	Not available	
	Secondary Sources (Wastewater)	-----[c]		——	
Dodecanedioic acid	Process Vents	-----[c]		-----[c]	
	Equipment Leaks	5.2 Mg/yr	(5.73)	5.2 Mg/yr.	(5.73)
	Secondary Sources	Not reported		——	
1,4-hexadiene	Process Vents	-----[c]		-----[c]	
	Equipment Leaks	53.8 Mg/yr	(59.3)	61.4 Mg/yr	(67.7)
	Secondary Sources	0		0	
Methylmethacrylate-butadiene-styrene resins	Process Vents	0.9 kg/Mg	(1.8)	8.6 kg/Mg	(17.2)
	Equipment Leaks	3.6 - 15.8 Mg/yr (n=2)	(4.0-17.4)	15.8 Mg/yr, not reported (n=2)	(17.4)
	Secondary Sources	0 (n=2)		0 (n=2)	
Sulfolane	Process Vents	-----[c]		-----[c]	
	Equipment Leaks	1.6 - 13.3 Mg/yr	(1.8-14.7)	1.6 - 13.3 Mg/yr	(1.8-14.7)
	Secondary Sources	Not reported		——	
Tetrahydrophthalic anhydride/acid	Process Vents	Not reported		——	
	Equipment Leaks	2.2 Mg/yr	(2.4)	2.2 Mg/yr	(2.4)
	Secondary Sources	0 (n=2)		0 (n=2)	

[a] Assumes production capacity = 100 percent. Values are in units of kg butadiene emitted per Mg product or, in the case of equipment leaks, Mg butadiene emitted per year. The numbers in parentheses are in units of pounds butadiene emitted per ton product (lbs/ton) or tons butadiene emitted per year (tons/yr).

[b] Ranges are based on actual emissions reported by the facilities. Thus, values include controls whenever they have been implemented.

[c] Not calculated because production capacity was not available.

(see Table 8), the procedure outlined in Appendix A was followed. Because information on emissions control through leak detection and repair programs is incomplete, adjustments to estimated emissions cannot be made. The only other controls in use were double mechanical pump seals and rupture discs on pressure relief devices. The emissions are in units of megagrams butadiene emitted per year (Mg/yr) and the equivalents in English units (tons/yr) are given in parentheses.

Based on information on secondary sources from eight facilities, emissions generally appear to be negligible from these sources, despite different end products. One exception is the butadiene-vinylpyridine process. The facility has estimated butadiene emissions from wastewater volatilization to be approximately 1.2 Mg/yr.[6]

Two estimates for emergency vent releases during upsets, startups, and shutdowns of the 1,4-hexadiene process are as follows: 0.2 Mg/yr (uncontrolled) off the abatement collection system for waste liquid and vapors and 43.1 Mg/yr from the reactor emergency vent. A brine refrigerated condenser on the reactor emergency vent may afford some emissions reduction but an efficiency has not been indicated.[1]

OTHER POTENTIAL BUTADIENE SOURCES

Specific information on indirect sources is limited to vinyl chloride monomer (VCM) and polyvinyl chloride (PVC) production processes. In VCM production, butadiene appears as an impurity in the final product at a maximum level of 6.0 parts per million (ppm).[14] An emission factor developed for overall production of PVC at a representative plant has been calculated and is given as 21×10^{-5} grams butadiene per kilogram PVC produced.

Some estimates for emissions from wastewater sent to POTWs by SB copolymer producers, considered a secondary source, have been made based on three industry responses to EPA Section 114 requests.[15] Using data on the butadiene content of wastewater sent to a POTW for each of these facilities and air emission models developed by EPA's Office of Air Quality Planning and Standards (OAQPS) for treatment, storage and disposal facilities estimated emissions for all three are 19 Mg/yr. This approach did not account for volatilization from wastewater during transport to the POTW.

Other potential sources have been identified by OAQPS which has collected information to assist State and local agencies in their air toxic programs. One document "Toxic Air Pollutant/Source Crosswalk: A Screening Tool for Locating Possible Sources Emitting Toxic Air Pollutants"[16] provides a list of possible sources for a number of toxic air pollutants. The Standard Industrial Classification (SIC) Codes identified in the report as possible butadiene sources are shown in Table 28.

Data collected by NIOSH during the 1972-1974 National Occupational Health (NOH) survey[17,18] identifies additional potential emission sources which are also listed in Table 28. The work was designed specifically to estimate the number of workers potentially exposed to butadiene grouped by SIC Code. In some cases the "potential exposure" determination was supported by observing butadiene in use. However, many of these cases are based on trade name product use; that is, the product used was derived from butadiene or may otherwise have a potential to contain butadiene.[17]

In a second, more recent NOH survey, 1981-1983,[19] six additional industries were identified as posing a potential for worker exposure. These are also included in Table 28. Because many SIC Codes have been revised, the one used in the study is given in parentheses after the SIC Code under which the catergory would be classified in 1989.

It is important to remember that these data were collected by NIOSH to assess worker exposure. These do not necessarily translate directly into atmospheric emission sources due to possible in-plant controls and butadiene removal as a result of its reactivity. However, the lists represent several

TABLE 28. POTENTIAL SOURCE CATEGORIES OF BUTADIENE EMISSIONS

1987 SIC Code[a]	1987 Description
2269*	Dyeing and finishing of textiles, except wool fabrics and unit-finishers of textiles, not elsewhere classified
2273 (2272**)	Carpets and rugs
2621***	Paper and allied products - paper mills
2631**	Paperboard mills
2652	Paperboard containers and boxes - set up paperboard boxes
2672***	Converted paper and paperboard products, except containers and boxes - coated and laminated paper, not elsewhere classified
2812*	Industrial inorganic chemicals - alkalis and chlorine
2813***	Industrial inorganic chemicals - industrial gases
2818***	Industrial inorganic chemicals - inorganic pigments
2819	Industrial inorganic chemicals - not elsewhere classified
2851	Paints, varnishes, lacquers, enamels, and allied products
2865*	Cyclic organic crudes and intermediates, and organic dyes and pigments.
2869*	Industrial organic chemicals, not elsewhere classified
2879*	Pesticides and agricultural chemicals, not elsewhere classified
2899	Chemicals and chemical preparations, not elsewhere classified
2911***	Petroleum refining
2951	Asphalt paving and roofing materials - paving mixtures and blocks
2992***	Miscellaneous products of petroleum and coal - lubricating oils and greases
2999***	Products of petroleum and coal - not elsewhere classified
3011	Rubber and miscellaneous plastics products - tires and inner tubes
3021*	Rubber and plastics footwear
3052[b] (3041)	Rubber and plastics hose and belting
3069[b] (3031)	Fabricated rubber products - not elsewhere classified
308, 3432 (3079)	Miscellaneous plastics products, plumbing fixtures fitting and trim
3357	Nonferrous wire drawing and insulating
3494	Miscellaneous fabricated metal products - valves and pipe fittings, not elsewhere classified
3499[b]	Fabricated metal products, not elsewhere classified
3533	Construction, mining, and material handling machinery and equipment - oil and gas field machinery

TABLE 28. (Continued)

1987 SIC Code[a]	1987 Description
3569	General industry machinery and equipment - not elsewhere classified
3585	Air-conditioning and warm air heating equipment and commercial and industrial refrigeration equipment
3621***	Electrical industrial apparatus - motors and generators
3643	Electric lighting and wiring equipment - current-carrying wiring devices
3651	Household audio and video equipment
3721	Aircraft and parts - aircraft
3799	Transportation equipment - not elsewhere classified
3841	Surgical and medical instruments and apparatus
3996	Linoleum, asphalted felt-base, and other hard surface floor coverings - not elsewhere classified
4226*	Special warehousing and storage, not elsewhere classified
4231***	Terminal and joint maintenance facilities for motor freight transportation
4612***	Pipelines, except natural gas - crude petroleum pipelines
5014**	Motor vehicles and motor vehicle parts and supplies - tires and tubes
5162, 5169	Chemicals and allied products - plastic materials and (5161*) basic forms and shapes, not elsewhere classified
5171***	Petroleum and petroleum products - petroleum bulk stations and terminals
5541	Gasoline service stations
6513	Real estate operators - apartment buildings
7319	Advertising - not elsewhere classified
7538**	Automotive repair shops - general
806	Hospitals
8372, 8741-8743 8748 (7392)	Commercial economic, sociological, and educational research, management, and public relations services except facilities support
8731 (7391**)	Research, development and testing services - commercial physical and biological research
8734***	Research, development, and testing services - testing laboratories

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[a] Those without an asterisk are from the NIOSH NOH 1972-1974 survey. The SIC Code in parentheses is the one used in the study, but it has since changed.

[b] SIC Code is listed by both EPA and NIOSH.

*SIC Code is listed as a potential source in the EPA "Crosswalk" document, Reference 16.

**SIC Code was identified as possible butadiene source during the NIOSH NOH 1981-1983 survey.

***SIC Code was identified from the Toxic Release Chemical Inventory Database for 1987 submittals by industry, Reference 19.

possible sources that may not otherwise be immediately identified as having a butadiene emissions potential.

A fourth reference for butadiene sources was the Toxic Chemical Release Inventory Data Base.[19] Industry reporting of butadiene releases for 1987 were identified by SIC Code and are included in Table 28.

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SECTION 8
SOURCE TEST PROCEDURES

1,3-Butadiene emissions can be measured by two methods: (1) EPA Reference Method 18, which was announced in the Federal Register on October 18, 1983;[1] and (2) NIOSH Analytical Method 1024 published in the NIOSH Manual of Analytical Methods on August 15, 1987.[2] EPA Reference Method 18 applies to the sampling and analysis of approximately 90 percent of the total gaseous organics emitted from an industrial source; whereas, NIOSH Method 1024 applies specifically to the collection and analysis of 1,3-butadiene. A third method has been developed and validated specifically to measure butadiene in vehicle exhaust.[3] Because of the more limited scope of application, no discussion of this method, a gas chromatography/flame ionization detector (GC/FID)-based method, will be presented.

EPA REFERENCE METHOD 18

In Method 18, a sample of the exhaust gas to be analyzed is drawn into a Tedlar® or aluminized Mylar® bag as shown in Figure 15. The bag is placed inside a rigid, leakproof container and evacuated. The bag is then connected by a Teflon® sampling line to a sampling probe (stainless steel, Pyrex® glass, or Teflon®) at the center of the stack. The sample is drawn into the bag by pumping air out of the rigid container.

The sample is then analyzed by gas chromatography (GC) coupled with flame ionization detection (FID). Based on recent field and laboratory validation studies, the recommended time limit for analysis is within 30 days of sample collection.[4] One recommended column is the 1.82 meter (6 feet) Supelco Porapak QS.[5] However, the GC operator should select the column and GC conditions that provide good resolution and minimum analysis time for 1,3-butadiene. Zero helium or nitrogen should be used as the carrier gas at a flow rate that optimizes the resolution.

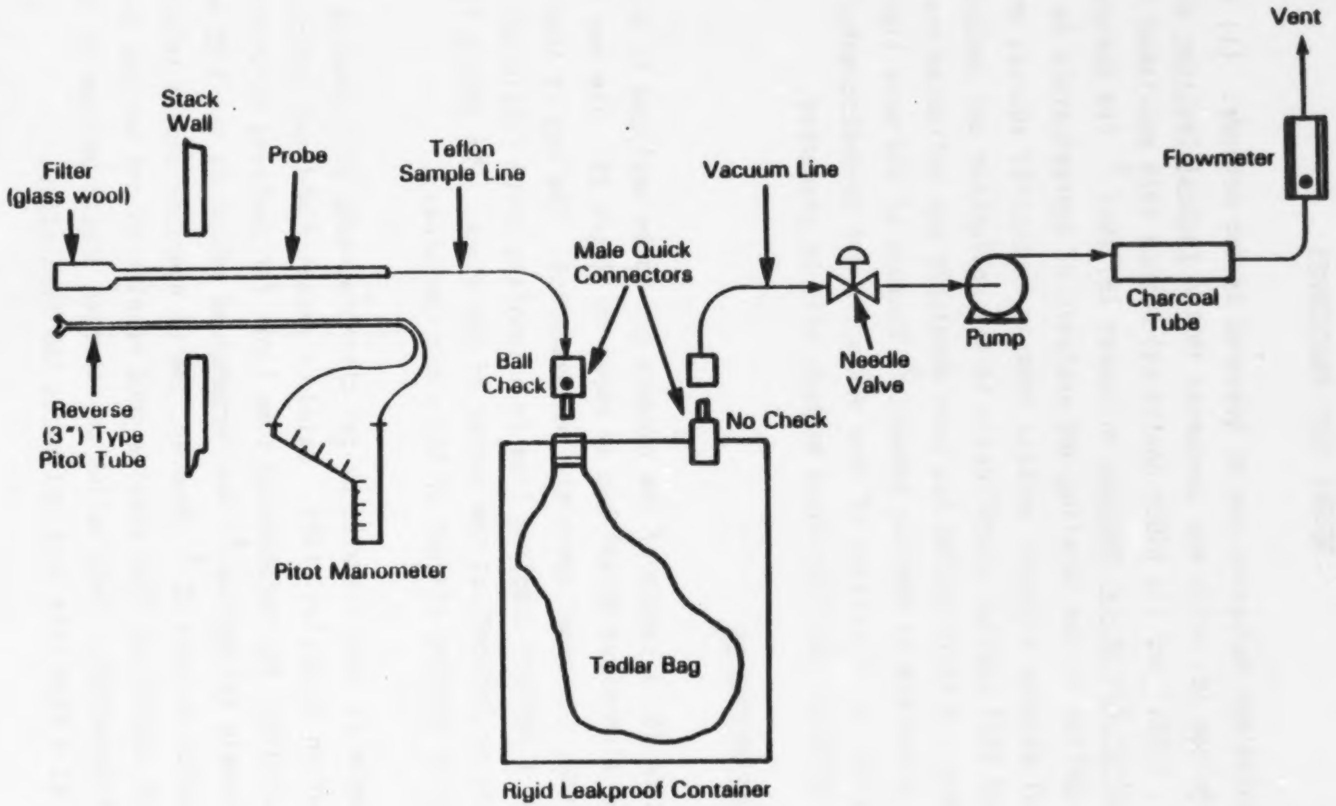
Vent
Stack
Wall
Filter
(glass wool)
Probe
Teflon
Sample Line
Vacuum Line
Flowmeter
Male Quick
Connectors
Charcoal
Tube
Pump
Needle
Valve
Ball
Check
No Check
Reverse
(3") Type
Pitot Tube
Pitot Manometer
Tedlar Bag
Rigid Leakproof Container
118172OR

Figure 15. Integrated Bag Sampling Train

The peak areas corresponding to the retention times of 1,3-butadiene are measured and compared to peak areas for a set of standard gas mixtures to determine the 1,3-butadiene concentrations. The detection limit of this method ranges from about 1 ppm to an upper limit governed by the FID saturation or column overloading. However, the upper limit can be extended by diluting the stack gases with an inert gas or by using smaller gas sampling loops.

Recent work by EPA's Atmospheric Research and Exposure Assessment Laboratory has produced a modified version of Method 18 for stationary source sampling.[6] One difference is in the sampling rate which is reduced to allow collection of more manageable gas volumes. The second introduces a filtering medium to remove entrained liquids; this improves the butadiene quantitation precision.

Two other changes involve the analytical procedure. The first uses picric acid in a second column (2 m x 1/8" stainless steel column, 0.19% picric acid on 80/100 mesh Carbopak C) to minimize the interference by butane and butene isomers which are also present in the stream. The second uses a backflush-to-vent configuration to remove any high boiling compounds that have been collected before they reach the picric acid column. These modifications allow more accurate quantitiation of butadiene to be performed in a short time period than with Method 18.

NIOSH METHOD 1024

In the NIOSH method, samples are collected with adsorbent tubes containing charcoal which has been washed and coated with 10 percent by weight 4-tert-butylcatechol (TBC-charcoal), a chemical known to inhibit the polymerization of 1,3-butadiene. Three-liter air samples should be collected with the use of a personal sampling pump at a flow rate of 0.05 L/minute.[2,7]

Samples are desorbed with carbon disulfide and analyzed by GC equipped with an FID and a column capable of resolving 1,3-butadiene from the solvent front and other interferences. The column specified in NIOSH Method 1024 is a 50 m x 32 mm internal diameter (ID) fused-silica, porous-layer, open-tubular (PLOT) column coated with aluminum oxide and potassium chloride (Al_2O_3/KCl).[2] Degradation of compound separation may be eliminated by using a back-flushable precolumn [i.e., 10 m x 0.5 mm ID fused-silica (CP Wax 57 CB)]. The precolumn allows light hydrocarbons to pass through, but water, methylene chloride, and polar or high boiling components are retained and can be backflushed.[2,6]

The amount of 1,3-butadiene in a sample is obtained from the calibration curve in units of micrograms per sample. Collected samples are sufficiently stable to permit six days of ambient sample storage before analysis. If samples are refrigerated, they are stable for 18 days. Butadiene can dimerize during handling and storage. The rate of dimerization is a function of temperature, increasing with increasing temperature. Consequently, samples should be stored at low temperatures.

This procedure is applicable for monitoring 1,3-butadiene air concentrations ranging from 0.16 ppm to 36 ppm. The GC column and operating conditions should provide good resolution and minimum analysis time.

REFERENCES FOR SECTION 8

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APPENDIX A

SAMPLE CALCULATIONS FOR EQUIPMENT LEAKS

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SAMPLE CALCULATIONS FOR EQUIPMENT LEAKS

An estimate of equipment leak emissions of butadiene depends on the equipment type (e.g., pump seals, flanges, valves, etc.), the associated emission factor, and the number of process components. For batch processes, the hr/yr that butadiene actually flows through the component is estimated from the reported percent of the year the equipment operates. For continuous processes, butadiene is assumed to flow through the equipment 8,760 hours per year.

The annual uncontrolled emission rate of butadiene from a specific equipment type is estimated by multiplying the following:

$$\begin{pmatrix}\text{\# equipment}\\ \text{components}\end{pmatrix} \times \begin{pmatrix}\text{weight \%}\\ \text{butadiene in}\\ \text{the stream}\end{pmatrix} \times \begin{pmatrix}\text{component}\\ \text{emission}\\ \text{factor}\end{pmatrix} \times \begin{pmatrix}\text{\# hours/yr}\\ \text{butadiene}\\ \text{in service}\end{pmatrix}$$

Component emission factors from Table 8 include controls in use by the facilities studied; therefore, SOCMI emission factors are used to estimate uncontrolled emissions. The resulting emissions estimate is adjusted for controls, where applicable, using the control efficiencies presented in Table 10 of the text.

Sample calculations are provided below to demonstrate the estimation procedure using information from Table A-1. Assuming continuous operation:

Emissions from Pump Seals

a) Mechanical

$$[(9 \times 0.025) + (2 \times 0.18)] \times 0.0494 \times 8{,}760 = 253 \text{ kg/yr}$$

TABLE A-1. DATA FOR SAMPLE CALCULATIONS

Equipment Type	Number of Components in Service Grouped by Average Weight Percent Butadiene <5%	5 - 10%	11 - 25%	SOCMI Emission Factor (kg/hr)	Controls	Control Efficiency (%)
Pump Seals-Mechanical	9	0	2	0.0494	---	---
Pump Seals-Double Mechanical	1	0	0	0	---	---
Pressure Relief Devices-Gas	7	50	2	0.104	Monthly LDAR[a]	51
Pressure Relief Devices-Liquid	6	0	0	0.104	Monthly LDAR	51

[a] LDAR means leak detection and repair program.

b) Double Mechanical

(1 x 0.025) x 0 x 8,760 = 0 kg/yr

c) Total Uncontrolled and Controlled = 253 kg/yr

Emissions from Pressure Relief Devices

a) Gas + Liquid - uncontrolled

[(13 x 0.025) + (50 x 0.075) + (2 x 0.18)] x 0.104 x 8,760

= 4,041 kg/yr

b) Gas + Liquid - controlled

4,041 x [1 - (51/100)] = 1,980 kg/yr

APPENDIX B

FACILITY-SPECIFIC EMISSIONS DATA FROM EPA SECTION 114 RESPONSES

APPENDIX B

FACILITY-SPECIFIC EMISSIONS DATA FROM EPA SECTION 114 RESPONSES

Tables B-1 through B-25 contain the capacity and emissions data that form the basis for the emission factor ranges and ranges of annual emissions presented in the preceding sections. Capacity data were compiled from responses to Section 114 requests or literature values if available. Most of the emissions data are from responses to Section 114 requests in 1984. Inconsistencies with the text are due to facility changes in ownership and/or in the production process since 1984. The emission values, therefore, may no longer reflect the current status of the industry. Furthermore, reported emissions were not supplied for every emission point identified. Nor were all emission points identified by each facility.*

Emission factors for each emission point were calculated by dividing the reported emissions by the facility's capacity, modified to reflect actual production. In instances where the use of facility production capacity in an emission factor might reveal company confidential information, the emissions data were not used to calculate the ranges. In the absence of facility-reported capacity values, literature values may have been used.

Equipment leak emission estimates were derived from 1984 data supplied by facilities in Section 114 responses. Using the procedure described in Appendix A and average CMA emission factors, ranges of annual emissions were calculated. Equipment count data for the miscellaneous category were unavailable, therefore estimates are based on the SOCMI emission factors as reported in the summary memoranda.

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*EPA is now actively collecting and receiving more recent information on emissions of 1,3-butadiene from industrial sources. These data could not be analyzed in sufficient time for their inclusion in this report, but will be evaluated for a potential future update. One observation is that the data becoming available indicate a higher level of control at facilities than previously was employed.

TABLE B-1. BUTADIENE PRODUCTION FACILITIES FOR WHICH 1984 EMISSIONS DATA ARE AVAILABLE[1]

Company	Location	Capacity (Mg/yr) in 1984
Amoco Chemicals Company	Chocolate Bayou, TX	82,000[a]
Arco Chemical Company	Channelview, TX	318,000
Cain Chemical Company[b]	Chocolate Bayou, TX	61,000[a]
Cain Chemical Company[c]	Corpus Christi, TX	100,000[a]
Exxon Chemicals Company	Baton Rouge, LA	141,000
Exxon Chemicals Company	Baytown, TX	109,000
Mobil Chemical Company	Beaumont, TX	27,000[a]
Shell Chemical Company	Deer Park, TX	363,000
Shell Chemical Company	Norco, LA	227,000
Texas Chemical Company	Port Neches, TX	163,000
Texas Petrochemicals Corporation	Houston, TX	363,000[d]

[a] Values taken from the literature.

[b] Formerly DuPont de Nemours and Company.

[c] Formerly El Paso Products Company.

[d] 227,000 Mg/yr from the recovery process, 136,000 Mg/yr from the dehydrogenation process.

TABLE B-2. BUTADIENE EMISSIONS (1984) FROM PROCESS VENTS AT OLEFINS AND BUTADIENE PRODUCTION FACILITIES[1]

Company	C_4 Stream Production Emissions (Mg/yr)[a]			Recovery Process Emissions (Mg/yr)[b]		
	Uncontrolled	Controlled	Control Device	Uncontrolled	Controlled	Control Device
Facility A	---[c]	---	---	---	---	Flare
Facility B	---	---	Flare	---	---	Flare
Facility C	---	---	---	---	---	Flare
Facility D	0.3	N/A[d]	None	---	---	---
Facility E	---	---	---	1.4	N/A	None
Facility F	---	---	---	---	---	Flare
Facility G	---	---	---	61.4	0.6	Boiler/Flare[e]
Facility H[f]	---	---	---	62.4	5.0[g]	Boiler/Flare

[a] C_4 stream production means production of a mixed C_4 stream as a coproduct from the manufacture of ethylene and other alkenes in an olefins plant.

[b] Recovery process means recovery of butadiene from a mixed C_4 stream.

[c] "---" means no information available.

[d] N/A means not applicable.

[e] The combination was assigned an overall efficiency of 99 percent.

[f] Source of the mixed C_4 stream is unknown.

[g] Reduction efficiency based on facility reported information.

TABLE B-3. SUMMARY OF BUTADIENE EMISSIONS (1987) FROM EQUIPMENT LEAKS AT NINE PRODUCTION FACILITIES[2]

Equipment Component	Number of Components	Emissions[a] (Mg/yr)	Emissions[a] (tons/yr)
Pumps - liquid	376	67	74
Compressors	17	0.0002	0.0002
Flanges	47,277[b]	46	51
Valves - gas	6,315	22	24
Valves - liquid	23,233	230	260
Pressure relief devices	428	41	45
Open-ended lines	1,744	0.67	0.73
Sample points[b]	40	0.34	0.37
	79,430[b]	410	460

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[a] Assumes 80 percent of production capacity (taken as 8760 hours of operations per year). Emissions rounded to two significant figures.

[b] Although only 11,428 flanges were included in the study, a ratio of 1.6:1 flanges:valves is generally accepted. The total number of flanges upon which the emission estimate is based is, therefore, [(6,315 + 23,233) x 1.6] = 47,277.

[c] Emission factor was taken from reference 2, p.5-16.

TABLE B-4. BUTADIENE EMISSIONS (1984) FROM SECONDARY SOURCES AT BUTADIENE PRODUCTION FACILITIES USING THE RECOVERY FROM A MIXED C_4 STREAM PROCESS[1]

	Emissions (Mg/yr)		Controls/Destination	
Company	Wastewater	Solid Waste	Wastewater	Solid Waste
Faciltiy B	Negligible[a]	Negligible[a]	---[b]	---
Facility D	5.5	---	Route emissions to flare, air strip or steam strip	Incineration
Facility E	0.03	Negligible[c]	Route emissions to flare, air strip or steam strip for recovery or to flare	Incineration
Facility G	---	---	Onsite NPDES, disposal wells	Offsite landfill
Facility H	16.4	---	Aeration lagoon	Offsite landfill
Facility I	0.16	---	Biological treatment	---
Facility J	290	---	Biological treatment, discharge	---
Facility K	---	---	Biological treatment	Landfill, disposal well

[a] Reported as "minor."

[b] "---" means no data available.

[c] Estimated at 3.99×10^{-5} Mg/yr.

TABLE B-5. STYRENE-BUTADIENE ELASTOMER AND LATEX PRODUCTION FACILITIES FOR WHICH 1984 EMISSIONS DATA ARE AVAILABLE[3]

Company	Location	Capacity (Mg/yr) in 1984[a]
Elastomer		
American Synthetic[b]	Louisville, KY	100,000
B. F. Goodrich[c]	Port Neches, TX	-----[d]
Copolymer Rubber	Baton Rouge, LA	211,000
Firestone	Lake Charles, LA	120,000
GenCorp	Odessa, TX	87,000
Goodyear	Houston, TX	-----
Uniroyal[c]	Port Neches, TX	183,000
Latex		
Borg-Warner[e]	Washington, WV	-----
Dow Chemical	Dalton, GA	-----
Dow Chemical	Freeport, TX	-----
Dow Chemical	Gates Ferry, CT	-----
Dow Chemical	Midland, MI	-----
Dow Chemical	Pittsburgh, CA	-----
GenCorp	Mogadore, OH	60,000
Goodyear[e]	Akron, OH	-----
Goodyear	Calhoun, GA	-----
W. R. Grace	Owensboro, KY	3,000
Polysar	Chattanooga, TN	152,000
Reichhold (DE)	Cheswold, DE	59,000
Reichhold (GA)	Kensington, GA	53,000
Unocal	La Mirada, CA	18,000

[a] Weight for elastomer is dry weight.

[b] Facility was mothballed in 1984.

[c] B.F. Goodrich and Uniroyal are now Ameripol Synpol.

[d] "-----" means company confidential.

[e] Facility operating status in 1988 unknown.

TABLE B-6. BUTADIENE EMISSIONS (1984) FROM PROCESS VENTS AT SB COPOLYMER PRODUCTION FACILITIES[3]

Company	Vent Location	Uncontrolled Emissions (Mg/yr)	Controlled Emissions (Mg/yr)	Control Device	Control Efficiency (%)
ELASTOMER					
Facility A	Recovery process	26	2.6	Absorber	90
Facility B	Butadiene recovery	420	21.0	Kerosene absorber	95
Facility C	Butadiene absorber vent	20[a]	0.02[a]	Boiler	99.9
Facility D	Tank farm, purification reactor, desolventization	80[b]	1.6[b]	Flare	98[c]
Facility E	Recovery area absorber vent	4.3	0.6	Absorber	86
Facility F	Process vessels (storage blending, coagulation, crumb washing)	60.0[a]	---	None	0
	Dryers	10.0[a]	---	None	0
Facility G	Butadiene recovery	126[b]	6.3[b]	Kerosene scrubbers	95
LATEX					
Facility H	Latex A1	115	---	None	0
	Latex A2	115	---	None	0
	Latex B	469.8	40.4	Pressure condenser	91.4
Facility I	Vent stack	---[d]	259	---	---
Facility J	Monomer mix tanks, recovery tank	---[d]	10.3	---	---
Facility K	Reactors, strippers	---[d]	9.8	---	---
Facility L	Process scrubber	---[d]	27.0	---	---
	Latex process	---[d]	4.8		

TABLE B-6. (Continued)

Company	Vent Location	Uncontrolled Emissions (Mg/yr)	Controlled Emissions (Mg/yr)	Control Device	Control Efficiency (%)
Facility M	Latex process and tanks	---[d]	5.1	---	---
Facility N	Central vacuum flare stack	570	11.4	Flare	98
	Latex stripping	0.5	---	None	0
Facility O	Butadiene recovery	33	3.3	Condenser	90
Facility P	Vent gas absorber	15	0.3	Scrubber	98
Facility Q	Reactor	95.0	---	None	0
	Mix tank	18.2	---	None	0
Facility R	Reactor recovery storage	5.0[e]	0.1	Flare	98[c]
	Recycle butadiene receiver	14.0[e]	---	None	0
	Stripping vacuum pump exhaust	40.8	---	None	0
Facility S	Process	295	5.9	Flare	98
Facility T	Waste vent gas	54.0	---	None	0
	Vacuum pump discharge	205.3	---	None	0
	Stream jet discharge	10.8	---	None	0
Facility U	Unknown	Unknown	Unknown	Incineration	Unknown

[a] Emissions shown are for both SB copolymer and nitrile rubber production.

[b] Emissions shown are for both SB copolymer and polybutadiene production.

[c] Facility reported a higher efficiency but did not support it with test data.

[d] Information for Dow facilities on control devices is considered confidential.

[e] Estimates exclude reported emissions for pressure relief discharges (0.1 Mg/yr).

TABLE B-7. BUTADIENE EMISSIONS (1984) FROM EQUIPMENT LEAKS AT SB COPOLYMER PRODUCTION FACILITIES[2,3]

Company	Uncontrolled Emissions (Mg/Yr)[a]	Control Status
Elastomer		
Facility A	5.6	PRDs[b] vented to a flare
Facility B	7.7	Rupture discs for PRDs
Facility C	13[c]	Rupture discs
Facility D	3.6	Rupture discs and flare for PRDs
Facility E	67	None reported
Facility F	21[c]	Rupture discs and flare for PRDs
Facility G	13[d]	Most PRDs have rupture discs vented
Latex		
Facility H	14	None reported
Facility I	4.5	None reported
Faciloty J	1.4	None reported
Facility K	0.89	None reported
Facility L	2.6	Some rupture discs
Facility M	1.9	Rupture discs
Facility N	5.3	None reported
Facility O	4.2	Rupture discs for PRDs
Facility P	4.3	None reported
Facility Q	0.10	None reported
Facility R	13	Some rupture discs
Facility T	2.0	Most PRDs have rupture discs

[a] Calculated using 1984 equipment counts and average CMA emission factor. Emissions rounded to two significant figures.

[b] PRDs= Pressure relief devices.

[c] The emissions are for both SB copolymer and nitrile rubber production.

[d] The emissions are for both SB copolymer and polybutadiene production.

TABLE B-8. BUTADIENE EMISSIONS (1984) FROM SECONDARY SOURCES AT SB COPOLYMER PRODUCTION FACILITIES (Mg/Yr)[3]

Company	Source			Waste Treatment
	Wastewater	Other Liquid Waste	Solid Waste	
Elastomer				
Facility A	0	0	0	None
Facility B	0.4	---[a]	---	Landfill, primary and secondary treatment
Facility C	0.8[b]	---	0.0006[b]	Biotreatment, incineration, landfill
Facility D	0	0	0	Unknown
Facility E	12.5[b]	---	2.0[b]	Biotreatment, landfill
Facility G	0	---	0	Unknown
Latex				
Facility H	0	0	0	Unknown
Facility I	0	---	0	NPDES permit, landfill
Facility J	0	---	0	Unknown
Facility K	0	0.007[c]	0	Biotreatment incineration of liquid waste, landfarm solids
Facility L	0	---	0	Biotreatment, landfill
Facility M	0	---	---	Solar pond
Facility N	0.00002	---	---	Equalization, settling, discharge to POTW
Facility O	13.1[d]	---[d]	---[d]	Discharge to POTW
Facility P	7.8	---	---	Aerated lagoon

TABLE B-8. CONTINUED

Company	Source			Waste Treatment
	Wastewater	Other Liquid Waste	Solid Waste	
Facility Q	Negligible[e]	---	---	Biotreatment, aerated lagoon
Facility R	24.0	---	---	City sewer[f]
Facility T	Negligible	Negligible	Negligible	Biotreatment

[a] "---" means no information available on the source.

[b] The emissions are for both SB copolymer and nitrile rubber production.

[c] Emissions occur off-site from an incinerator stack.

[d] Facility did not report emissions separately for each of the four production processes on-site.

[e] "Negligible" means only trace amounts of butadiene reported in waste.

[f] Polysar has two units in production; waste treatment at Unit #2 is confidential.

TABLE B-9. POLYBUTADIENE PRODUCTION FACILITIES FOR WHICH 1984 EMISSIONS DATA ARE AVAILABLE[4]

Company	Location	Capacity (Mg/Yr) in 1985
American Synthetic Rubber	Louisville, KY	63,000[a]
Arco Chemical[b]	Channelview, TX	6,800
Borg-Warner	Ottawa, IL	------[c]
Firestone	Orange, TX	110,000[a]
Firestone	Lake Charles, LA[d]	
Goodyear	Beaumont, TX	------[c]
Phillips	Borger, TX	64,000[a]
Polysar	Orange, TX	------[c]

[a] Value taken from the literature.

[b] Facility operating status in 1988 unknown.

[c] Company confidential.

[d] Facility coproduces SBS elastomer and polybutadiene rubber, but is primarily dedicated to SB elastomer.

TABLE B-10. BUTADIENE EMISSIONS (1984) FROM PROCESS VENTS AT POLYBUTADIENE PRODUCTION FACILITIES[4]

Company	Vent Locations	Uncontrolled Emissions (Mg/yr)	Controlled Emissions (Mg/yr)	Control Device	Control Efficiency (%)
Facility A	Recovery process	0.08	0.002	Butadiene absorber, flare	97.5
Facility B	Acetone column vent	33.1	---	None	---
	Vacuum system vent	66.2	---	None	---
Facility C	Flashers	44.4	4.0	Butadiene recovery	91
Facility D	Plantwide	20	0.4	Flare	98[a]
Facility E	Two plant vents	515	10.3	Flare	98[a]
Facility F	Polymerization reactors	5	0.1	Flare	98
	Kerosene scrubbing	25	0.5	Flare	98

[a] Plant reported greater than 98 percent control efficiency, but did not provide supporting test data.

TABLE B-11. BUTADIENE EMISSIONS (1984) FROM EQUIPMENT LEAKS AT POLYBUTADIENE PRODUCTION FACILITIES[2,4]

Company	Uncontrolled Emissions (Mg/Yr)[a]
Facility A	3.7
Facility B	5.3
Facility D	29
Facility E	9.5
Facility F	5.2
Facility G	4.4

---

[a] Calculated using 1984 equipment counts and average CMA emission factors. Emissions rounded to two significant figures.

TABLE B-12. BUTADIENE EMISSIONS (1984) FROM SECONDARY SOURCES AT POLYBUTADIENE PRODUCTION FACILITIES (Mg/yr)[a,4]

Company	Source		Waste Treatment
	Wastewater	Solid Waste	
Facility B	---	0	Landfill
Facility C	0	---[a]	Activated sludge
Facility F	19.3	---[b]	Lagoon

[a] Facility lists as a source but provides no data.

[b] "---" means no information available on the source.

TABLE B-13. ADIPONITRILE PRODUCTION FACILITIES FOR WHICH 1984 EMISSIONS DATA ARE AVAILABLE[5]

Company	Capacity (Mg/yr) in 1984
Facility A	210,000[a]
Facility B	132,900

[a] Value taken from the literature.

TABLE B-14. BUTADIENE EMISSIONS (1984) FROM PROCESS VENTS
AT ADIPONITRILE PRODUCTION FACILITIES[5]

Company	Vent Location	Uncontrolled Emissions (Mg/yr)	Controlled Emissions (Mg/yr)	Control Device	Control Efficiency (%)
Facility A	Recycle purge	490	9.8	Flare	98[a]
	Butadiene dryer	---[b]	---	Boiler	---
Facility B	Recycle purge	330	6.6	Flare	98[b]
	Butadiene dryer	4.4	0.004	Boiler	99.9
	Jets	---	---	Boiler	99.9
	Second reactor	---	---	Boiler	99.9
	Refining	---	---	Boiler	99.9

[a] Facility reported a higher efficiency but did not provide supporting test data.

[b] "---" means information not available.

TABLE B-15. BUTADIENE EMISSIONS (1984) FROM EQUIPMENT LEAKS AT ADIPONITRILE PRODUCTION FACILITIES[2,5]

Company	Uncontrolled Emissions (Mg/yr)[a]	Controls
Facility A	4.8	Ambient monitoring,[b] double mechanical seals, some PRDs[c] routed to a flare.
Facility B	2.5	Quarterly LDAR,[d] ambient monitoring, double mechanical seals.

[a] Calculated using 1984 equipment counts and average CMA emission factors. Emissions rounded to two significant figures.

[b] Ambient monitoring in the vicinity is used to detect elevated VOCs, potentially indicating leaks.

[c] PRDs means pressure relief devices.

[d] LDAR means leak detection and repair program.

TABLE B-16. BUTADIENE EMISSIONS (1984) FROM SECONDARY SOURCES AT ADIPONITRILE PRODUCTION FACILITIES[5]

Company	Source Description	Uncontrolled Emissions (Mg/yr)
Facility A	Waste tank	2.0
	Butadiene separator blowdown water	---[a]
Facility B	Sump tank[b]	---
	Waste liquids[b]	---
	Wastewater	0.9

[a] "---" means not reported. Value taken from the literature.

[b] Both sources are routed to a boiler with 99.9 percent reduction efficiency.

TABLE B-17. CHLOROPRENE/NEOPRENE PRODUCTION FACILITIES FOR WHICH 1984 EMISSIONS DATA ARE AVAILABLE[6]

Company	Capacity (Mg/yr) in 1985[a]
Facility A	34,000
Facility B	43,000

[a] Values taken from the literature.

TABLE B-18. BUTADIENE EMISSIONS (1984) FROM NEOPRENE PRODUCTION FACILITIES[6]

		Process Vent Emissions (Mg/yr)				
Company	Vent Location	Uncontrolled	Controlled	Control Device	Control Efficiency (%)	Equipment Leaks (Mg/yr)[a] Uncontrolled
Facility A	DCB refining	4.8	---	None	0	0.93
	DCB refining	0.87	0.1	Absorber/ -20°F condenser	88.6	
	DCB refining	0.96	0.5	-20°F condenser	48.0	
Facility B	DCB refining	160	---	Water-cooled condenser	0	4.4
	DCB synthesis	360	7.2	Flare	98[b]	

---

[a] Calculated using 1984 equipment counts and average CMA emission factors. Emissions rounded to two significant figures.

[b] Company estimated a higher efficiency but did not provide supportive data.

TABLE B-19. ACRYLONITRILE-BUTADIENE-STYRENE RESIN PRODUCTION FACILITIES FOR WHICH 1984 EMISSIONS DATA ARE AVAILABLE[7]

Company	Location	Capacity (Mg/Yr) in 1985[a]
Goodyear[b]	Akron, OH	150
Monsanto	Addyston, OH	161,000
Monsanto	Muscatine, IA	52,200

[a] Values taken from the literature.

[b] Goodyear coproduces ABS with nitrile elastomer. About 3 percent is dedicated to production.

TABLE B-20. BUTADIENE EMISSIONS (1984) FROM ABS PRODUCTION FACILITIES[7]

	Process Vent Emissions (Mg/yr)					
Company	Vent Location	Uncontrolled	Controlled	Control Device	Control Efficiency (%)	Equipment Leaks (Mg/yr)[a] Uncontrolled
Facility A	Spray dryer[b]	0.8	---	None	0	Unknown
	Dewatering (1)	Unknown	---	None	0	
Facility B	Polymerization (9)	500	0.5	Flare	99.9	3.2
	Dewatering (1)	<10	<0.01	Boiler	99.9	
	Dewatering (1)	1.9	---	None	0	
	Dewatering (1)	1.9	---	None	0	
	Tanks (3)	9.0	---	None	0	
	Tanks (6)	Unknown	---	Unknown	---	
	Coagul/wash (7)	Unknown	---	Unknown	---	
	Compounding (9)	0	---	None	0	
Facility C	Polymerization (1)	250	2.5	Flare	99	1.1
	Polymerization (1)	6.2	---	None	0	
	Coagul/wash (2)	16.8	---	None	0	
	Dewatering (4)	9.7	---	None	0	
	Compounding (1)	6.3	---	None	0	
	Tanks (5)	5.6	---	None	0	

[a] Calculated from 1984 equipment counts and average CMA emission factors. Emissions rounded to two significant figures.

[b] Number in parentheses indicates the number of vents.

TABLE B-21. NITRILE ELASTOMER PRODUCTION FACILITIES FOR WHICH 1984 EMISSIONS DATA ARE AVAILABLE[7]

Company	Location	Capacity (Mg/Yr dry rubber or latex) in 1985
B. F. Goodrich	Akron, OH	0[a]
Copolymer	Baton Rouge, LA	6,800[b]
Goodyear	Houston, TX	16,000
Goodyear[c]	Akron, OH	5,000
Sohio[d]	Lima, OH	---[e]
Uniroyal Chemical Co.	Painesville, OH	16,300

[a] B. F. Goodrich closed its 14,000 Mg/yr NBR facility in 1983. Facility still produces 7,600 Mg/yr of vinyl pyridine.

[b] Value taken from the literature.

[c] Facility also produces about 150 Mg/yr of ABS copolymer (3 percent of production.

[d] Facility operating status in 1988 unknown.

[e] "---" means company confidential.

TABLE B-22. BUTADIENE EMISSIONS (1984) FROM NITRILE ELASTOMER PRODUCTION FACILIITES[7]

Company	Vent Location	Process Vent Emissions (Mg/yr) Uncontrolled	Process Vent Emissions (Mg/yr) Controlled	Control Device	Control Efficiency (%)	Equipment Leaks (Mg/yr)[a] Uncontrolled
Facility A	Process A (46)[b]	55	2.2	Boiler	96	---[c]
Facility B[d]	Butadiene absorber	<0.06	<0.001	Boiler	99+	17
Facility C[e]	Blowdown tank (1)	32	3.2	Condenser	90	---
	Coagulator (1)	38.4	---	Chemical treatment[f]	Unknown	
	Building (1)	2.9	---	None	0	
	Screening (1)	---	---	Chemical treatment[f]	Unknown	
	Dewatering (1)	---	---	None	0	
	Dryer (2)	---	---	None	0	
Facility D[g]	Reactor (1)	---	---	Flare	99.9	---
	Absorber (1)	---	---	Flare	99.9	
	Distillation (1)	---	---	Flare	99.9	
	Screen/coagulation (2)	15	1.5	Steam stripper for acrylonitrile	90	
Facility E	Reactor (1)	200	0.2	Thermal oxidation	99.9	0.39
Facility F[h]	Recycle receiver (1)	3.0	0.33	Scrubber	89	6.5
	Steam jets (2)	---	---	Steam stripper for acrylonitrile	90	
	Dryer (1)	---	---	Steam stripper for acrylonitrile	90	
	Tanks (8)	---	---	Steam stripper for acrylonitrile	90	

[a] Calculated from 1984 equipment counts and average CMA emission factors. Emissions rounded to two significant figures.

[b] Number in parentheses indicates the number of Vents of this type.

[c] "---" means information not available.

[d] Facility is also an SB copolymer producer; total facility emissions reported. Emissions apportioned to NBR production based on percent production resulting in nitrile elastomer--three percent.

[e] Facility is also an ABS copolymer producer; total facility emissions were reported. Emissions apportioned to NBR production based on percent production resulting in nitrile elastomer--97 percent.

[f] Chemical treatment destroys residual acrylonitrile. The effect on butadiene is not known.

[g] Only equipment leaks emissions are apportioned using percent of capacity dedicated to nitrile elastomer.

[h] Facility is also an SB copolymer producer; total facility emissions were reported. Emissions apportioned to NBR production based on percent production resulting in nitrile elastomer--five percent

TABLE B-23. MISCELLANEOUS USES OF BUTADIENE FOR WHICH EMISSIONS DATA ARE AVAILABLE[5]

Company	Location	Product	Mode of Operation	1986 Design Capacity (Mg/yr)
ArChem Company	Houston, TX	Tetrahydrophthalic (THP) Anhydride	Batch	515
B. F. Goodrich Company	Akron, OH	Butadiene-vinylpyridine Latex	Batch (on demand)	___[a]
Denka (Mobay Synthetics Corporation)	Houston, TX	THP Acid	Batch	1,500
DuPont	Beaumont, TX	1,4-Hexadiene	Continuous	---[b]
DuPont	Victoria, TX	Dodecanedioic Acid	Continuous (2 weeks per month due to low demand)	---
Kaneka Texas Corporation	Bayport, TX	MBS Resins	Batch	13,000[d]
Phillips Chemical Company	Borger, TX	Butadiene Cylinders[c]	Batch	485
		Butadiene-furfural Cotrimer[c]	Continuous, intermittent, about 65% of the time	45
		Sulfolane	Batch	___
Rohm and Haas Company	Louisville, KY	MBS Resins	Batch	---
Shell Oil Company	Norco, LA	Sulfolane	Unknown	___
Union Carbide	Institute, WV	Butadiene Dimers	Continuous	6,500

[a] "___" capacity not known.

[b] "---" means company confidential.

[c] In operation in 1984, status unknown in 1987.

[d] According to reference 4, capacity was due to increase to 24,000 Mg/yr in 1987.

TABLE B-24. BUTADIENE EMISSIONS FROM PROCESS VENTS ASSOCIATED WITH MISCELLANEOUS USES OF BUTADIENE[5,8,9]

Chemical Produced	Company	Vent Location	Uncontrolled Emissions (Mg/yr)	Controlled Emissions (Mg/yr)	Control Device	Control Efficiency (%)
Butadiene cylinders	Facility A	Process vents	10.5	---	None	0
Butadiene dimers	Facility B	Feedpot, recycle pot, reactor, and three recovery stills	5	0.1	Flare	98
Butadiene-furfural cotrimer	Facility A	Reactor	Unknown	0	By-product butadiene dimer recovery	100
		Crude storage	9.9	---	None	0
Butadiene-vinylpyridine latex	Facility C	Process vents	320	0.32	Boiler	99.9
		Dryer	6.0	---	None	0
Dodecanedioic acid	Facility D	Butadiene dryer + two jets	<100	<0.1	Boiler	99.9
		Reactor	200	0.2	Boiler	99.9
1,4-Hexadiene	Facility E	Knockout pot	24.7	---	None	0
		Reactor, stripper, recycle condenser	Unknown	Unknown	Abatement collection system for waste liquids and vapors routed to a boiler	99.9
Methyl methacrylate-butadiene-styrene resins	Facility F	Reactor	100	0.1	Boiler	99.9
		Coagulator	6.0	---	None	0
		Dryer	6.0	---	None	0
	Facility G	Reactor	0.9	---	None	0
Sulfolane	Facility H	Reactant recycle accumulator	1.57	0.031	Flare	98
		Light ends stripper	6.87	0.14	Flare	98
Sulfolane	Facility A	Caustic scrubber	90	---	None	0
		Sulfolene flakes caustic scrubber	29.3	---	None	0
		Sulfolane reactor	0	---	None	0

TABLE B-25. BUTADIENE EMISSIONS FROM EQUIPMENT LEAKS ASSOCIATED WITH MISCELLANEOUS USES OF BUTADIENE[5,8,9]

Chemical Produced	Company	Uncontrolled Emissions (Mg/yr)	Controlled Emissions (Mg/yr)	Controls	Control Efficiency (%)
Butadiene cylinders	Facility A	<0.1	---	None	0
Butadiene dimers	Facility B	3.9[a]	---	Ambient monitoring[b], double mechanical seals	0, 100
Butadiene-furfural cotrimer	Facility A	0.5[c]	---	Rupture discs	100
Butadiene-vinylpyridine latex	Facility C	Unknown	0.55	Quarterly LDAR[d], some rupture discs	32, 100
1,4-Hexadiene	Facility D	61.4[e]	53.8	Some double mechanical seals, some rupture discs, some closed sampling	___[f]
Dodecanedioic acid	Facility E	5.2	---	Visual inspections[g]	0
Methyl methacrylate-butadiene-styrene resins	Facility F	3.6	---	Unknown	---
	Facility G	15.8	---	Ambient monitoring[b]	0
Sulfolane	Facility A	13.3	---	None	0
	Facility H	1.6	---	None	0
Tetrahydrophthalic anhydride/acid	Facility I	2.2	---	Visual inspections[g]	0

[a] Excludes pumps with double mechanical seals.

[b] Ambient monitoring in the vicinity is used to detect elevated VOC levels, a potential indication of equipment leaks.

[c] Excludes pressure relief devices since all are controlled.

[d] LDAR means leak detection and repair program.

[e] Excludes pumps with double mechanical seals and closed sampling ports.

[f] Each control is 100 percent effective; however, since not all components are controlled, overall reduction is not equal to 100 percent.

[g] For visual inspections, no reduction is given due to inadequate information.

REFERENCES FOR APPENDIX B

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2. Randall, J. L. et al., Radian Corporation. Fugitive Emissions from the 1,3-butadiene Production Industry: A Field Study. Final Report. Prepared for the 1,3-Butadiene Panel of the Chemical Manufacturers Association. April 1989. p. 5-11.

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7. Memorandum from R. Burt and R. Howle, Radian Corporation, to L. B. Evans, EPA/Chemicals and Petroleum Branch, January 29, 1986. Estimates of Acrylonitrile, Butadiene, and Other VOC Emissions and Controls for ABS and NBR Facilities.

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